

# PATENT ABSTRACTS OF JAPAN

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(71)Applicant : DAINIPPON INK & CHEM INC

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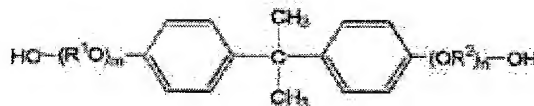
(72)Inventor : OGURA KATSUYUKI  
NAKAMURA MASANOBU

(54) ELECTROSTATIC CHARGE IMAGE DEVELOPING COLOR TONER AND METHOD FOR MANUFACTURING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a red color toner, particularly a magenta toner having excellent coloring power and hue, showing stable electrification characteristics even when the environment such as temperature and humidity changes, having excellent color reproducing property and showing stable and high printing picture quality, good fixing property, and excellent offset resistance.

SOLUTION: In the electrostatic charge image developing color toner containing a binder resin and a coloring agent, the binder resin contains a polyester resin obtained by the reaction of (A) one kind or more of polybasic acid compounds selected from a group consisting of polybasic acids and acid anhydrides having a valency of  $\geq 2$  or lower alkylesters of these and (B) aliphatic alcohol having a valency of  $\geq 2$ . The coloring agent is one kind or more of organic pigments selected from C.I.Pigment Red 150, 31, 147, 176, 187, 188 and 269.



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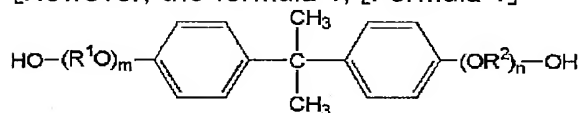
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## CLAIMS

[Claim(s)]

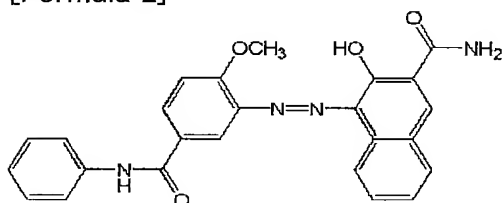
[Claim 1]It is the main ingredients about one or more sorts of polybasic acid compounds chosen from a group which said binder resin becomes from polybasic acid, acid anhydrides, and these lower alkyl ester more than (A) divalent in color toner for electrostatic charge image development containing binder resin and colorant, and fatty alcohol more than (B) divalent.

[However, the formula 1, [Formula 1]



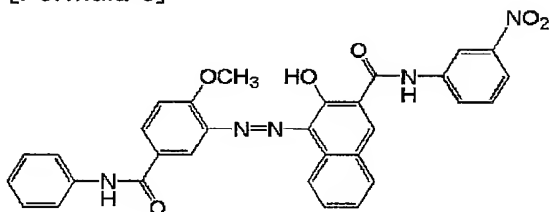
(Formula 1)

(among a formula, R<sup>1</sup> and R<sup>2</sup> are the same or different, ethylene or a propylene group is shown, m and n are the same or different, and the integer of 0-7 is shown, and m+n shows the integer of 0-7.) --] except the compound which has a bisphenol skeleton expressed The polyester resin which carries out, and is produced by making react is contained, and said colorant is the formula 2, the formula 3, the formula 4, the formula 5, the formula 6, the formula 7, and the formula 8, [Formula 2]



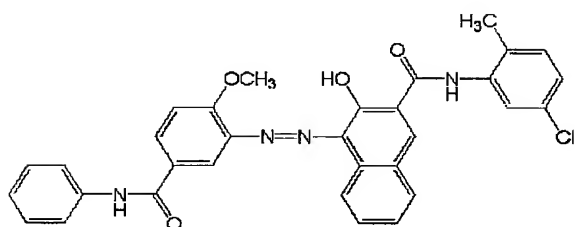
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[Formula 3]



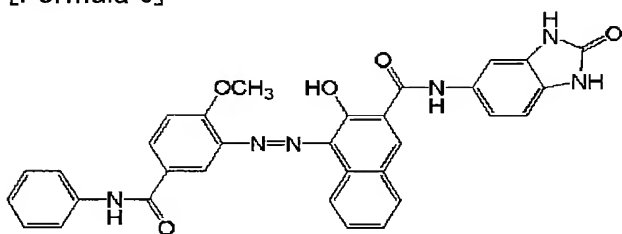
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[Formula 4]



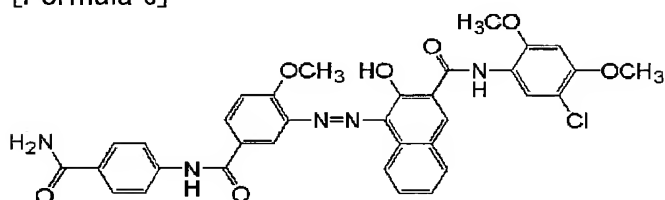
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[Formula 5]



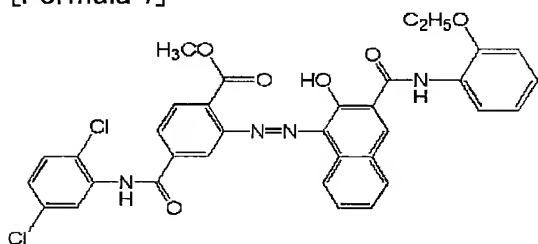
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[Formula 6]



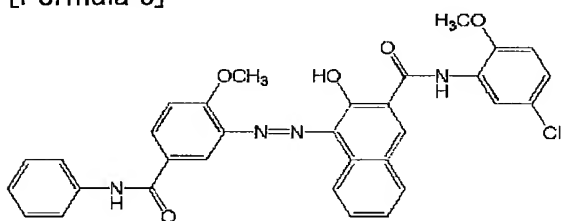
(Formula 6)

[Formula 7]



(Formula 7)

[Formula 8]



(Formula 8)

Color toner for electrostatic charge image development being one sort or the organic color beyond it chosen from \*\*.

[Claim 2]The color toner for electrostatic charge image development containing a release agent according to claim 1.

[Claim 3]The color toner for electrostatic charge image development according to claim 2 which is a wax in which said release agent contains a higher fatty acid ester compound and/or an aliphatic alcohol compound.

[Claim 4]The color toner for electrostatic charge image development containing a charge

controlling agent according to claim 1.

[Claim 5] A manufacturing method of color toner which carries out diluent powder of one sort or an organic color beyond it chosen from said formula 2, the formula 3, the formula 4, the formula 5, the formula 6, the formula 7, and the formula 8 using said binder resin further after performing distributed processing beforehand using said some of binder resin.

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[Translation done.]

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to color toner for electrostatic charge image development for developing the electrostatic charge image in electro photography, electrostatic recording, electrostatic printing, etc., and a manufacturing method for the same.

[0002]

[Description of the Prior Art] As a toner composition for obtaining a visible image by a xerography, many things which many made distribute black colorant like carbon black in binder resin are used. However, these days, the color toner which distributed cyanogen paints, a magenta pigment, a yellow pigment, or other chromatic color paints in the binder is also used, and the copying machine of full color or a mono color and printer using these color toner are developed.

[0003] As the characteristic required of such color toner, It has the clear color reproduction nature which demonstrates the transparency outstanding in the color pile at the time of performing that the picture after printing has vivid color enhancement, and process printing, and color turbidity does not produce, Or when the color picture obtained by carrying out transfer and fixing on the over head projector (henceforth OHP) sheet is projected on a screen, color reproduction characteristics, such as copying out a clear color without muddiness, are searched for.

[0004] Conventionally, much art is indicated about such color toner, and especially about a magenta color or red color toner, C.I.PIGMENT RED 122 which is the paints of a quinacridone series as an organic color, or C.I.PIGMENT RED 57:1 which is a lake color have mainly been used. Although hue is good and excellent in the color reproduction nature of a blue system, the dispersibility of the former over resin for toners is bad, and it is inferior in tinting strength. Therefore, in order to print the target concentration, content in a toner must be increased, and as a result, it has the fault that the electrifying characteristic of a toner becomes unstable easily. When it was easy to become positive triboelectric charging especially as paints and applied to a negative triboelectric charging toner, there was a problem that electrification quantity fell while in use.

[0005] In the latter, although tinting strength is good, since Ca salt structure is taken, it is hygroscopic and there is a fault that the electrifying characteristic of a toner tends to receive environmental influence. When it was used for printer's ink, the clear magenta color was acquired, but when it was used for a toner, C.I.PIGMENT RED 57:1 tends to become magenta color [ of yellow ], and was inferior as hue compared with C.I.PIGMENT RED 122.

[0006] In the toner field from such a background, Even if it has the outstanding tinting strength and hue and changes environment, such as temperature and humidity, the stable electrifying characteristic is shown and as the result, It excelled in color reproduction nature, also when it applied to a negative triboelectric charging toner further, while using it, electrification quantity was not changed, but to obtain the red color toner in which good and stable printing image quality is shown, especially magenta toner has been desired.

[0007] Although the heat roll fixing system is generally widely used as a method established in a

toner image, the good fixability and offset-proof nature in that case are also the important characteristic for which color toner is asked. In the latest color copying machine or a printer, improvement in the speed of processing speed is performed, and fixing temperature is becoming low temperature with a fixing time nearby short time more. Therefore, in the latest color toner, it being established more with low temperature and low energy, and having offset-proof nature in a wide temperature requirement is called for with the improvement of the aforementioned color reproduction nature and an electrifying characteristic.

[0008]

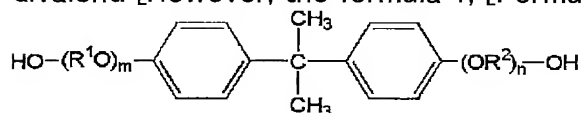
[Problem(s) to be Solved by the Invention] Even if the purpose of this invention has the outstanding tinting strength and hue and it changes environment, such as temperature and humidity, It excels in color reproduction nature, as the result, the stable electrifying characteristic is shown, also when it applies to a negative triboelectric charging toner further, while using it, electrification quantity is not changed, but it is in providing the red color toner in which good and stable printing image quality is shown, especially magenta toner.

[0009] It is in other purposes of this invention providing the red color toner which showed good fixability also on a low energy fixing condition like low temperature fixation or short-time fixing, and was excellent also in offset-proof nature, especially magenta toner.

[0010] Other purposes of this invention are to provide the manufacturing method of the red color toner with which it is satisfied of the above-mentioned characteristic, especially magenta toner.

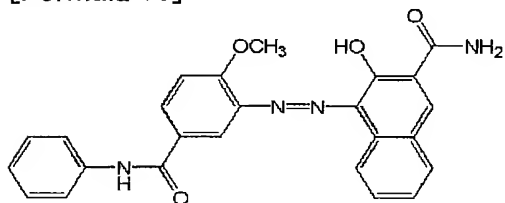
[0011]

[Means for Solving the Problem] This invention persons came to complete this invention, as a result of repeating research wholeheartedly that above-mentioned SUBJECT should be solved. Namely, in color toner for electrostatic charge image development in which this invention contains binder resin and colorant, Said binder resin is the main ingredients about one or more sorts of polybasic acid compounds chosen from a group which consists of polybasic acid, acid anhydrides, and these lower alkyl ester more than (A) divalent, and fatty alcohol more than (B) divalent. [However, the formula 1, [Formula 9]



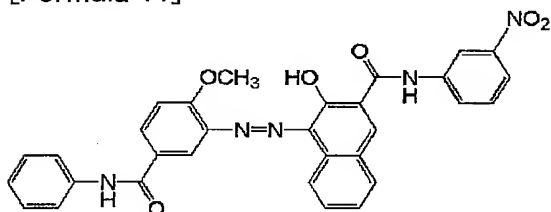
(Formula 1)

(among a formula,  $\text{R}^1$  and  $\text{R}^2$  are the same or different, ethylene or a propylene group is shown,  $m$  and  $n$  are the same or different, and the integer of 0-7 is shown, and  $m+n$  shows the integer of 0-7.) --] except the compound which has a bisphenol skeleton expressed The polyester resin which carries out, and is produced by making react is contained, and said colorant is the formula 2, the formula 3, the formula 4, the formula 5, the formula 6, the formula 7, and the formula 8, [Formula 10]

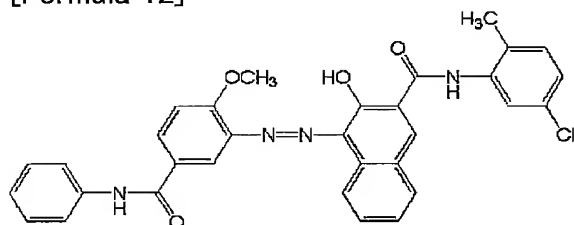


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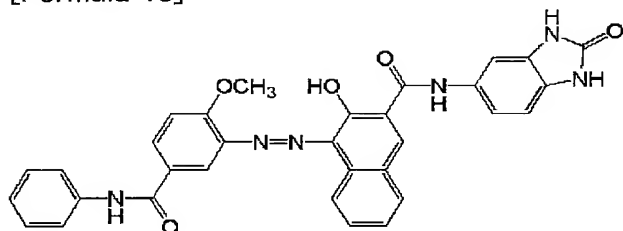
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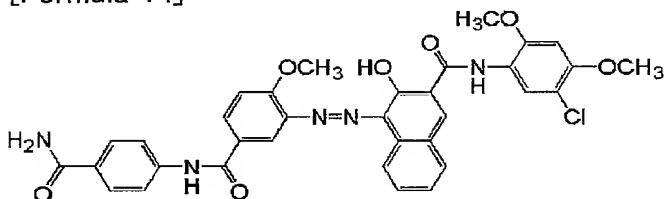
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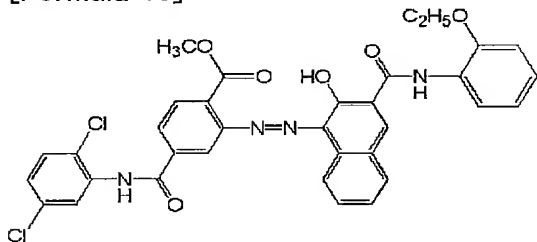
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[Formula 13]



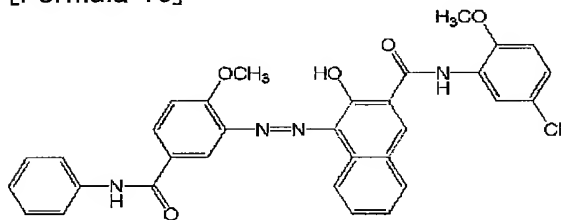
(Formula 5)  
[Formula 14]



(Formula 6)  
[Formula 15]



(Formula 7)  
[Formula 16]



(Formula 8)

The color toner for electrostatic charge image development being one sort or the organic color beyond it chosen from \*\* is provided.

[0012] Said some of binder resin is used for this invention for one sort or the organic color beyond it chosen from said formula 2, the formula 3, the formula 4, the formula 5, the formula 6, the formula 7, and the formula 8, After performing distributed processing beforehand, the

manufacturing method of the color toner which carries out diluent powder using said binder resin further is provided.

[0013]

[Embodiment of the Invention] Hereafter, this invention is explained in detail. The binder resin used for the color toner for electrostatic charge image development of this invention is polyester resin.

[0014] As a polybasic acid compound (A) chosen from the polybasic acid, the acid anhydrides, and/or these lower alkyl ester more than divalent for manufacturing the polyester resin used by this invention, For example, phthalic anhydride, terephthalic acid, isophthalic acid, orthophthalic acid, Naphthalene dicarboxylic acid, adipic acid, maleic acid, a maleic anhydride, Fumaric acid, itaconic acid, citraconic acid, hexahydro phthalic anhydride, Tetrahydro phthalic anhydride, cyclohexanedicarboxylic acid, succinic acid, Dicarboxylic acid, such as malonic acid, glutaric acid, azelaic acid, and sebacic acid, the derivative of those, or its esterification material, Polyvalent carboxylic acid of three or more organic functions, such as trimellitic acid, trimellitic anhydride, pyromellitic acid, and pyromellitic dianhydride, the derivative of those, or its esterification material is mentioned, for example.

[0015] As fatty alcohol (B) more than divalent, For example, 1,4-cyclohexane dimethanol, ethylene glycol, A diethylene glycol, triethylene glycol, propylene glycol, Dipropylene glycol, tripropylene glycol, butanediol, Pentanediol, hexandiol, a polyethylene glycol, a polypropylene glycol, Ethylene oxide propylene oxide random copolymer diol, Ethylene oxide propylene oxide block copolymer diol, Diol, such as ethylene oxide tetrahydro franc copolymer diol and poly KAPUROKAKU ton diol, Sorbitol, 1,2,3,6-hexanetetraol, 1, 4-sorbitan, Pentaerythritol, 1,2,4-butanetriol, 1 and 2, 5-pentanetriol, Polyhydric alcohol of three or more organic functions, such as glycerin, isobutane triol, 2-methyl-1,2,4-butanetriol, trimethylolethane, trimethylolpropane, and 1,3,5-TORIMECHI roll benzene, is mentioned.

[0016] The compound which has two or more glycidyl groups can also be used into one molecule as fatty alcohol (B) more than divalent [ reacted to the carboxylic acid compound of the above (A) ]. Specifically, there are neopentyl glycol diglycidyl ether, glycerol triglycidyl ether, trimethylolpropane triglycidyl ether, trimethylolethane triglycidyl ether, pentaerythritol tetraglycidyl ether, etc., for example.

[0017] In this invention, aromaticdiol or polyhydric alcohol more than trivalent can also be used together in the range which does not affect performance. As aromaticdiol or polyhydric alcohol more than trivalent, For example, catechol, resorcinol, hydroquinone, a bisphenol A type epoxy resin, bisphenol F type epoxy resin, a bisphenol smooth S form epoxy resin, cresol novolak type epoxy resin, phenol novolak type epoxy resin, etc. are mentioned. However, the compound which has a bisphenol A skeleton expressed with the above-mentioned formula 1 is removed. As aromaticdiol removed, for example Bisphenol A, polyoxyethylene (2.2)-2,2-bis(4-hydroxyphenyl)propane, Polyoxyethylene (2.0)-2,2-bis(4-hydroxyphenyl)propane, Polyoxypropylene (2.0)-2,2-bis(4-hydroxyphenyl)propane, Polyoxypropylene (2.2)-polyoxyethylene (2.0)-2,2-bis(4-hydroxyphenyl)propane, Polyoxypropylene (6)-2,2-bis(4-hydroxyphenyl)propane, Polyoxypropylene (2.2)-2,2-bis(4-hydroxyphenyl)propane, Polyoxypropylene (2.4)-2,2-bis(4-hydroxyphenyl)propane, polyoxypropylene (3.3)-2,2-bis(4-hydroxyphenyl)propane, these derivatives, etc. are mentioned.

[0018] By using fatty alcohol more than divalent in this invention, the chain of polyester resin becomes flexible, When it mixes with a career and the toner using such polyester resin is used as a two component developer, there is an effect which eases the stress which a career receives within a developer, it prevents the resin coating phase of a carrier surface exfoliating, and the effect that the life of a developer is prolonged as a result is acquired. The share received when it uses as a toner for one ingredient of nonmagnetic development and a toner passes through between a developing sleeve and charge members can be eased, and it can be considered as a high durability developer.

[0019] When a polyester main chain elasticity-izes, the fixability in low temperature is improved. Although adding a wax in a toner is a means generally used, in order to improve fixing / offset performance, Especially in polyester resin using fatty alcohol more than divalent [ in this



invention ], the compatibility of waxes is good and the fixing performance and offset-proof nature in low temperature are improved further.

[0020]Therefore, it is necessary to use the above-mentioned aromaticdiol in the range which does not spoil the main point of this invention. As for the quantity using the above-mentioned aromaticdiol, it is desirable that it is less than 30 mol % to all the alcohol components. It is less than 20 mol % more preferably.

[0021]As carboxylic acid components used by this invention, dimethyl naphthalate, diethyl naphthalate, dibutyl naphthalate, etc. are more suitably used as naphthalene dicarboxylic acid and/or its lower alkyl ester. These compounds need to use more than 1 mol % of a total acid component, and are more than 5 mol % more preferably.

[0022]A monomer including naphthalene ring structure has an effect in raising Tg of resin, and its heat-resistant cohesiveness of resin improves. In the system which used elastic fatty alcohol for the subject especially as an alcohol component, the fall of Tg of resin can be suppressed and resin having both the low temperature fixability by using fatty alcohol more than divalent and the heat-resistant cohesiveness by naphthalene dicarboxylic acid can be obtained.

[0023]Polyester resin in this invention can be obtained by performing a dehydrating condensation reaction or an ester exchange reaction using the above-mentioned raw material component (A) and (B), for example under existence of a catalyst. Although in particular the reaction temperature and reaction time in this case are not limited, they are usually 2 to 24 hours at 150–300 °C.

[0024]Composition of such polyester resin can also be performed by adding a catalyst. As an esterification catalyst to be used, the organic metal like dibutyltin dilaurate and dibutyl tin oxide, the metal alkoxide like tetrabutyl titanate, etc. are mentioned, for example. A transesterification catalyst can be used when the carboxylic acid components to be used are lower alkyl ester. As a transesterification catalyst, zinc acetate, lead acetate, metal acetate like magnesium acetate or a zinc oxide, the metallic oxide like antimony oxide, or the metal alkoxide like tetrabutyl titanate is mentioned, for example. About the addition of a catalyst, it is preferred to consider it as 0.01 to 1% of the weight of the range to the total amount of raw material.

[0025]Although the glass transition temperature (Tg) of the polyester resin used for this invention has a not less than 50 °C preferred thing, the Tg of especially a not less than 55 °C thing is preferred especially. Below 50 °C, Tg tends to produce blocking high (heat condensation), when a toner is exposed under an elevated temperature inside preservation, conveyance, or the developer of a machine.

[0026]as softening temperature of the polyester resin used for this invention, the thing of the range of 90 °C – 180 °C is preferred also in not less than 90 °C — it is the range of 95 °C – 160 °C more preferably. When softening temperature is less than 90 °C, a toner tends to produce isoagglutination and it is easy to become a trouble in the time of preservation, or the case of printing, and in exceeding 180 °C, fixability worsens in many cases.

[0027]when the transparency at the time of making it especially established on the color reproduction nature at the time of a color pile or an OHP sheet is required as full color toner, as softening temperature of polyester resin, the thing of the range of 90 °C – 130 °C is preferred — it is the range of 95 °C – 120 °C more preferably.

[0028]As acid value of polyester resin of this invention, it is preferred that they are 20 or less mgKOH/g at the point that the moisture resistance of a toner becomes good.

[0029]T1/2 temperature measured using Shimadzu flow tester CFT-500 which is a constant stress extrusion type small tube type rheometer defines the softening temperature of resin in this invention. The measuring condition in the flow tester was performed on with piston cross-section area <sup>2</sup> of 1 cm, cylinder pressure 0.98MPa, die 1 mm in length, the diameter of a die hole of 1 mm, measurement start temperature 50°C, heating-rate C/min of 6 degrees, and a sample weight of 1.5 g conditions.

[0030]Although it is used in this invention out of the organic color expressed with said formula 2, the formula 3, the formula 4, the formula 5, the formula 6, the formula 7, and the formula 8, choosing one sort or more than it, The magenta pigment usually used with the conventional

toner by using these paints, For example, the color toner which has good tinting strength, story tonality, definition, and transfer property as compared with the C.I.Pigment Red 122 grade which are C.I.Pigment Red 57:1 and a quinacridone pigment can be obtained. When continuous printing is carried out, a stable electrification behavior can be shown, and the high-definition picture excellent in color reproduction nature and transparency can be printed.

[0031]The Color Index number of the above-mentioned organic color is as follows.

The organic color of the formula 2; C.I.Pigment. The organic color of the Red 150 formula 3; C.I.Pigment. The organic color of the Red 31 formula 4; C.I.Pigment. The organic color of the Red 147 formula 5; C.I.Pigment. organic color [ of the Red 176 formula 6 ]; -- organic color [ of the C.I.Pigment Red 187 formula 7 ]; -- organic color [ of the C.I.Pigment Red 188 formula 8 ]; -- in C.I.Pigment Red 269 this invention, It is preferred to use the organic color expressed with the formula 2 and/or the formula 8 also in the above. It is more preferred to use the organic color expressed with the formula 2.

[0032]The amount of the organic color used expressed with the formula 2 in this invention, the formula 3, the formula 4, the formula 5, the formula 6, the formula 7, and the formula 8 has the preferred range of one to 50 weight section per binder resin 100 weight section, its range of two to 30 weight section is more preferred, and especially its range of two to 20 weight section is preferred.

[0033]In addition to the above-mentioned organic color, in the range which does not lose the effect of this invention, since hue is adjusted, others and colorant can be added and used in this invention. As such colorant, although a well-known thing is raised, For example, as colorant of a blue system the C.I.Pigment Blue 60 grade of C.I.Pigment Blue 15-3 of a phthalocyanine system and an indanthrone system, As reddish colorant. C.I.Pigment of a \*\* quinacridone series. Red 122 and azo C.I.Pigment. Red 22, C.I.Pigment Red23, C.I.Pigment Red31, C.I.Pigment Red48:1, C.I.Pigment Red 48:3, and C.I.Pigment Red 57:1 grade as colorant of a yellow system. C.I.Pigment Yellow12 of \*\* azo, C.I.Pigment Yellow 13, C.I.PigmentYellow 14, C.I.Pigment Yellow 17, and C.I.Pigment. There are Yellow 97, C.I.Pigment Yellow 155, C.I.Pigment Yellow151 of a benz imidazolone system, C.I.Pigment Yellow 154, C.I.Pigment Yellow 180, etc.

[0034]The above quoted paints can be used together with the organic color of the formula 2 - the formula 8 in the range which does not spoil the purpose of this invention. For example, by combining with yellow system paints, it can also be made the toner of a LGT color system and can also be considered as the toner of a blue-purple color system by combining with cyan color system paints. The magenta toner which has a clear magenta color with tinting strength can be obtained by using together with the red pigment of the blueness of C.I.Pigment Red 122, C.I.Pigment Red 23, and C.I.Pigment Red31 grade especially.

[0035]When using together the paints of the formula 2 - the formula 8, and other paints, as for the amount of the paints used of the formula 2 - the formula 8, 40 % of the weight or more is preferred to the content of the whole paints, and it is 50 % of the weight or more more preferably.

[0036]Although publicly known various waxes, for example, polypropylene wax, polyethylene wax, a polyamide system wax, the Fischer Tropsch wax, etc. can be suitably used for the toner of this invention as a release agent until now, It is preferred to use the wax which contains a higher fatty acid ester compound and/or an aliphatic alcohol compound especially as a release agent.

[0037]Also in the wax containing a higher fatty acid ester compound and/or an aliphatic alcohol compound, natural wax, such as carnauba wax, a montan ester wax, a rice wax, and a scale insect wax, and/or especially a synthetic ester system wax are preferred. Especially as a synthetic ester system wax, tetrabehenic acid ester of pentaerythritol is preferred.

[0038]These waxes show good dispersibility to especially polyester resin, and their improvement of fixability and offset-proof nature is remarkable. these waxes -- many -- also in several sheets and prolonged printing, For example, without adhering to the charge members forced on the developing sleeve, when it uses as a toner for one ingredient of nonmagnetic development, electrification stable in the toner is given, there is neither an image defect nor a greasing, and printing of a high-definition and high definition picture is attained. When it uses with one sort or the organic color beyond it chosen from said formula 2 used by this invention - the formula 8

and is considered as color toner, the color toner which was excellent in transparency as compared with the wax of a hydrocarbon system like polypropylene wax is obtained. The color toner which has such the characteristic is transparent, and fits printing to the OHP sheet in which a skillful projection picture is called for, and the use which prints two or more colors in piles, and prints the neutral colors of good color reproduction nature.

[0039]It is preferred to use the de-free fatty acid carnauba wax which removed free fatty acid by refining as carnauba wax. As acid value of de-free fatty acid carnauba wax, three or less are preferred and it is two or less acid value more preferably. From conventional carnauba wax, de-free fatty acid carnauba wax serves as micro crystallite, and its dispersibility in the inside of polyester resin improves. A montan ester wax is refined from a mineral, and serves as micro crystallite like carnauba wax by refining, and its dispersibility in the inside of polyester resin improves. It is preferred that it is 30 or less as acid value especially in a montan ester wax. A rice wax refines a rice bran low and, as for acid value, it is preferred that it is 13 or less. the wax in which the larva of a scale insect (alias IBOTAROU MUSHI) secretes a scale insect wax — it can obtain by melting the \*\* ingredient in boiling water, for example, and carrying out after-separation cooling solidification of the upper layer, or repeating it. The scale insect wax refined by such a means is white in a solid state, shows the very sharp melting point, and is suitable as a wax for toners in this invention. Acid value becomes ten or less by refining, and five or less are preferred as an object for toners.

[0040]The above-mentioned wax may be used independently, or it may combine, it may be used, and good fixing offset performance is obtained by carrying out 1-30 weight-section content preferably 0.3 to 40 weight section to binder resin. It is one to 20 weight section more preferably. If less than 0.3 weight sections, offset-proof nature will be spoiled, and if more than 40 weight sections, the mobility of a toner will worsen, By adhering to a carrier surface in a two-ingredient development system, it is generated by the SUPENTO career, and it will have an adverse effect on the electrifying characteristic of a toner, or will adhere to the layer thickness regulating member welded by pressure to the developing roll in one ingredient of nonmagnetic development system.

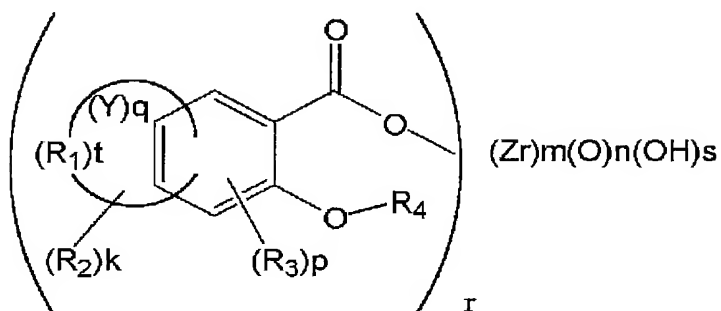
[0041]In this invention, a charge controlling agent can be used if needed. As a right charge controlling agent, for example, a nigrosine series color, triphenylmethane dye, Resin containing quarternary ammonium salt, the 4th class ammonium, and/or an amino group, etc., As a negative electrification controlling agent, a trimethyl ethane system color, the metallic complex of salicylic acid, The metallic complex of benzoic acid, a copper phthalocyanine, perylene, Quinacridone, There are resin containing heavy metal content acid dye, such as azo pigment, metallic complex azo dye, and an azochromium complex, a calyx allene type phenol system condensate, an annular polysaccharide, a carboxyl group, and/or a sulfonyl group, etc.

[0042]It is desirable to use a colorless charge controlling agent in this invention especially, As a negative charge controlling agent, as a metal complex compound of salicylic acid, "BONTORON E-84" by an Orient chemicals company. "TN105" by the Hodogaya chemicals company and "N4PVP-2481" by Clariant, LTD. etc. As a colorless right charge controlling agent, TP-302 of quarternary-ammonium-salt structure, TP-415, TP-610; (product made from the Hodogaya chemicals), BONTORON P-51; (product made from Orient chemicals), the copy charge PSY (Clariant Japan), etc. are used suitably. "FCA-201-PS" (FUJIKURA KASEI CO., LTD.) etc. is mentioned as a positive triboelectric charging resin mold charge controlling agent containing the 4th class ammonium and/or an amino group.

[0043]Especially, as a charge controlling agent which can be especially used conveniently in this invention, there are a compound of the following formula 9 and a compound of the formula 10.

<Formula 9> [0044]

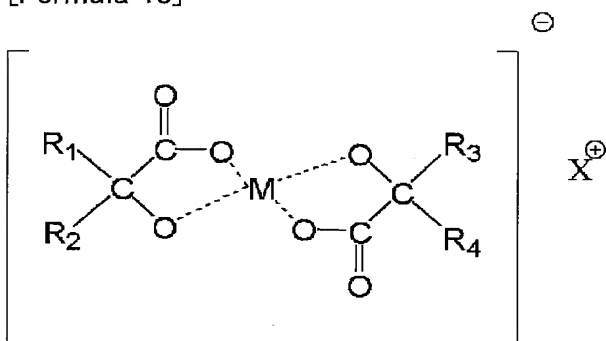
[Formula 17]



$R_1$  is the 4th class carbon, methine, and methylene among a formula — N and S. A hetero atom of O and P may be included and Y expresses cyclic structure connected with a saturated bond or an unsaturated bond, Mutually  $R_2$  and  $R_3$  independently An alkyl group, an alkenyl group, An aryl group, an aryloxy group or an aralkyl group which may have an alkoxy group and a substituent, or an aralkyloxy group, An amino group, a carboxyl group which may have a halogen group, hydrogen, a hydroxyl group, and a substituent, A carbonyl group, a nitro group, a nitroso group, a sulfonyl group, and a cyano group are expressed,  $R_4$  expresses hydrogen or an alkyl group and t 0 thru/or an integer of 1–12, m — as for an integer of 0 thru/or 1–4, and q, an integer of 0 thru/or 1–20 and k are [ an integer of 1 to 20, and n / an integer of 0 thru/or 1–4, and p / an integer of 1 to 20 and s of an integer of 0 thru/or 1–3 and r ] the integers of 0, or 1 thru/or 20.

[0045]<Formula 10> [0046]

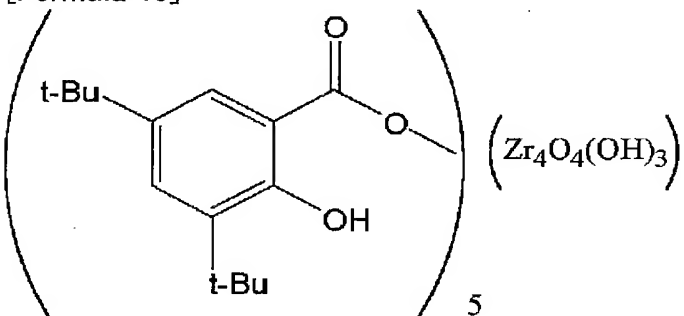
[Formula 18]



the inside of a formula,  $R_1$ , and  $R_4$  — a hydrogen atom and an alkyl group. Substitution or an unsubstituted aromatic ring (a condensed ring is also included) is shown,  $R_2$  and  $R_3$  show substitution or an unsubstituted aromatic ring (a condensed ring is also included), M shows one sort of trivalent metal chosen from B, aluminum, Fe, Ti, Co, and Cr, and  $X^+$  shows a cation. [0047] As a concrete example of a compound of <the formula 9>, there is following < charge controlling agent 1>- <charge controlling agent 3>.

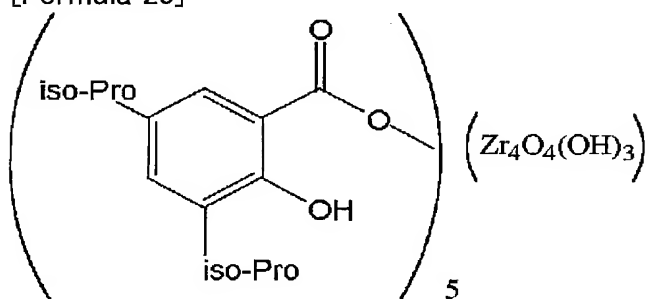
[0048]<Charge controlling agent 1> [0049]

[Formula 19]



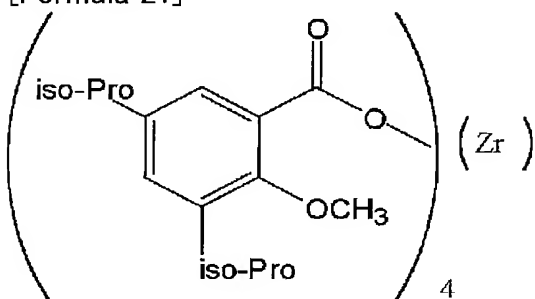
[0050]&lt;Charge controlling agent 2&gt; [0051]

[Formula 20]



[0052]&lt;Charge controlling agent 3&gt; [0053]

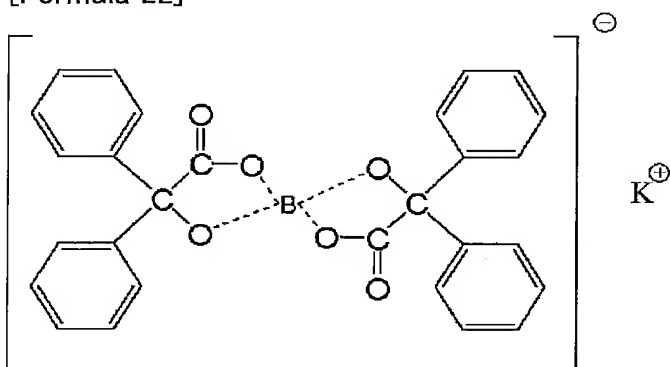
[Formula 21]



[0054]As a concrete example of the compound of <the formula 10>, there are the following <charge controlling agents 4> and the <charge controlling agent 5>.

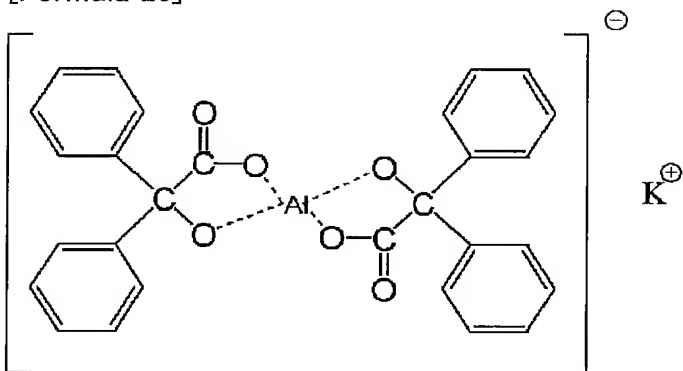
[0055]&lt;Charge controlling agent 4&gt; [0056]

[Formula 22]



[0057]&lt;Charge controlling agent 5&gt; [0058]

[Formula 23]



[0059]The above-mentioned charge controlling agent may be used independently, or it may combine, it may be used, and good electrification performances are obtained by carrying out 0.5-5 weight-section content preferably 0.3 to 15 weight section to binder resin.

[0060]Although it can therefore obtain for arbitrary means of publicly known common use, after carrying out melt kneading of a wax and the various additive agents, for example to resin and colorant if needed above the melting point (softening temperature) of resin, a manufacturing method for obtaining a toner of this invention can be ground, and can be obtained by classifying. in order to make an effect of this invention reveal further, it is good to distribute some binder resin which uses one sort or an organic color beyond it chosen from said formula 2 - the formula 8 at high concentration, and to carry out diluent powder to binder resin which uses this dispersed matter after that.

[0061]Thus, as a process which makes binder resin distribute colorant beforehand at high concentration, a publicly known method, i.e., the masterbatch method, a flushing process, etc., can be used conventionally. The masterbatch method is a method of obtaining a good dispersed matter, by kneading colorant with resin at high concentration using a kneader or a roll mill, applying a high share. A flushing process is a method of obtaining a dispersed matter of high pigment concentration, carrying out heat kneading of a hydrous paste and binder resin of paints with a pressurized kneader, replacing water and binder resin, and removing moisture.

[0062]As for a rate of binder resin in this dispersed matter of high pigment concentration, and colorant, it is preferred that the amount of coloring matters is in ten weight sections - 100 weight sections to binder resin 100 weight section.

[0063]It mixes by a kneading means of 2 rolls, 3 rolls, a pressurized kneader, or a biaxial extruder by using concrete for example, above-mentioned resin and colorant as an essential ingredient. Under the present circumstances, although colorant should just distribute uniformly in resin and conditions in particular of that melt kneading are not limited, they are usually 10 minutes - 2 hours at 80-180 \*\*.

[0064]Coarse grinding aiming at mitigation of load in a pulverizing process and improvement in the efficiency of comminution is performed if needed. Although in particular a device and conditions that are used for coarse grinding are not limited, it is common to carry out coarse grinding to particle diameter below a 3-mm mesh pass with ROTOPU REXX, a PARUPE riser, etc.

[0065]Subsequently, it pulverizes with air type grinders, such as mechanical grinders, such as a turbo mill and KURIPU TRON, a whorl type jet mill counter jet mill, and a collision plate type jet mill, and a method of classifying with a pneumatic elutriation machine etc. is mentioned. What is necessary is to choose and just to set up pulverizing and a device of a classification, and conditions become desired particle diameter, particle size distribution, and particle shape.

[0066]In this invention, various additive agents (it is called an external additive) can be used for surface treatment of toners, such as fluid improvement in a toner, and electrifying characteristic improvement. As an external additive which can be used by this invention, For example, a silicon dioxide, titanium oxide, oxidation aluminum, cerium oxide, a zinc oxide, Non-subtlety granular materials, such as tin oxide and zirconium oxide, and them Silicone oil, What carried out the surface treatment by hydrophobing processing agents, such as a silane coupling agent, polystyrene, Resin pulverized coal, such as an acrylic, a styrene acrylic, polyester, polyolefine, cellulose, polyurethane, benzoguanamine, melamine, nylon, silicone, phenol, and vinylidene fluoride, etc. are used.

[0067]A silicon dioxide (silica) which carried out hydrophobing processing of the surface by various kinds of polyorganosiloxanes and hexamethylenedisilazane, a silane coupling agent, etc. also in these can use conveniently especially. There are some which are marketed with the following trade names as such a thing, for example.

[0068]AEROSIL R972, R974, R202, R805, R812, RX200, RY200, R809, RX50, RA200HS, RA200H [Japanese Aerosil, Inc.]

WACKER HDK H2000, H1018, H2050EP, HDKH3050EP, HVK2150 [Wacker Chemicals yeast AJIA, Inc.]

Nipsil SS-10, SS-15, SS-20, SS-50, SS-60, SS-100, SS-50B, SS-50F, SS-10F, SS-40, SS-70, SS-72F, [Japanese Silica Industry]

CABOSIL TG820F, TS-530, TS-720 [Cabot Specialty Chemicals ink]

[0069]Particle diameter of an external additive is 1/10 or less desirable especially suitably [ that it is 1/3 or less / of a diameter of a toner ]. These external additives may use together two or more sorts of different mean particle diameter.

[0070]By using together a thing of particle diameter size, and a thing of particle diameter smallness in a toner for one ingredient of nonmagnetic development especially, toner flow kinesis and development durability are raised, the long-term stability of adherence to a braid of a developing machine and prevention of fogging, and electrification at the time of running, etc. are acquired, and it is desirable.

[0071]A using rate of an external additive is 0.1 to 3 % of the weight preferably 0.05 to 5% of the weight to matrix toner 100 weight section.

[0072]Said silica can be performed to particle toner as a method of carrying out externally adding, for example using a Henschel mixer etc. which are the usual mixers for granular materials, and what is called surface treatment machines, such as a hybridizer. It may be made for silica to make this externally adding process adhere on the surface of particle toner, and a part of silica may be made to be embedded at particle toner.

[0073]Color toner for electrostatic charge image development of this invention can be used as an object for the development of an electrostatic latent image by a xerography as a two component developer mixed with the one-ingredient developer, one ingredient of nonmagnetic developer, or a career. There is no restriction in particular in a kind of career, and a career which carried out the resin coat to iron powder of publicly known common use, a ferrite, magnetite, etc. and them is used.

[0074]Although the core agent of a career can use iron powder used for the usual two-ingredient development system, magnetite, a ferrite, etc., since true specific gravity is low, high resistance, and is excellent in environmental stability and it is easy to make it into a globular form especially, a ferrite with good mobility or magnetite is used suitably. Especially the shape of a core agent cannot interfere a globular form, an infinite form, etc., and can use them. Although mean particle diameter is generally 10-500 micrometers, in order to print high resolution images, 30-80 micrometers is preferred.

[0075]As coating resin which covers these core agents, For example, polyethylene, polypropylene, polystyrene, polyacrylonitrile, Polyvinyl acetate, polyvinyl alcohol, a polyvinyl butyral, Polyvinyl chloride, a polyvinyl carbazole, polyvinyl ether, polyvinyl ketone, VCM/PVC/vinyl acetate copolymer, styrene/acrylic copolymer, straight silicone resin that consists of an ORGANO siloxane bond, or its denaturation article, A fluoro-resin, an acrylic resin (meta), polyester, polyurethane, polycarbonate, phenol resin, amino resin, melamine resin, benzoguanamine resin, a urea resin, amide resin, an epoxy resin, acrylic polyol resin, etc. can be used. Also in these, especially silicone resin, a fluoro-resin, and an acrylic resin (meta) are excellent in electrifying stability, covering intensity, etc., and can use it more conveniently. That is, as for a resin coated carrier used by this invention, it is preferred that it is the resin coating magnetic carrier covered with one or more sorts of resin chosen from silicone resin, a fluoro-resin, and an acrylic resin (meta) using a ferrite or magnetite as a core agent.

[0076]When using color toner for electrostatic charge image development of this invention as a toner for one ingredient of nonmagnetic development, it is preferred to use as a toner for one ingredient of nonmagnetic development of a contact type. One ingredient of nonmagnetic developing method of a contact type is a method of developing an electrostatic latent image which carried out frictional electrification and was formed subsequently to the surface of a photo conductor, when a toner passes through between a developing sleeve and layer thickness regulating members welded by pressure to it.

[0077]In this case, especially if it is anticipated-use conditions, construction material of an electrification grant member of a developer, etc. will not be limited. For example, a developing sleeve made of aluminum, stainless steel, urethane rubber, and silicone rubber, aluminum, stainless steel, duralumin, copper, or a layer thickness regulating member that pasted urethane

rubber and silicone rubber together to them can use it conveniently.

[0078]Composition of a developer which was suitable in order that color toner for electrostatic charge image development of this invention might reveal an effect when it used as a toner for one ingredient of nonmagnetic development, Either of a developing sleeve and a layer thickness regulating member is a case where it is metal, such as aluminum and stainless steel, and the most effective combination (a developing sleeve/layer thickness regulating member), It is the combination of a layer thickness regulating member of combination of a developing sleeve made of urethane rubber or silicone rubber, and a layer thickness regulating member made from stainless steel, a developing sleeve made from stainless steel and urethane rubber, or a product made of silicone rubber.

[0079]

[Example]Hereafter, this invention is explained still in detail using working example and a comparative example. The numerical value in a presentation table expresses a "weight section" below. The synthetic example of the binder resin which was used in preparing a toner first is shown below.

(Synthetic example 1)

Naphthalene-dicarboxylic-acid 87 weight-section terephthalic acid 249 weight-section diethylene-glycol 26 weight-section neopentyl glycol 104 weight-section ethylene glycol 50 weight-section tetrabutyl titanate the raw material of 2.5 or more weight sections. It put into the 4 Thu mouth flask glass [ 2L ], and the thermometer, the stirring rod, and the nitrogen introducing pipe were attached, it decompressed one by one after a 10-hour reaction at 240 \*\* under the ordinary pressure nitrogen air current in the electric heat mantle heater, and the reaction was continued by 10mmHg. The reaction was pursued by the softening temperature according to ASTM-E 28-517, and when softening temperature amounted to 101 \*\*, it ended the reaction. The obtained polymer (it expresses the resin A hereafter) was a colorless solid, and the acid value 7, the glass transition temperature of 70 \*\* by a DSC measurement method, and softening temperature were 102 \*\*.

[0080](Synthetic example 2)

Terephthalic acid 315 weight-section diethylene-glycol 21 weight-section cyclohexane dimethanol 144 weight-section ethylene glycol 50 weight-section tetrabutyl titanate It reacted like the example 1 of resin composition using the raw material of 2.5 or more weight sections. The obtained polymer (it expresses the resin B hereafter) was a colorless solid, and the acid value 9, the glass transition temperature of 60 \*\* by a DSC measurement method, and softening temperature were 97 \*\*.

[0081]

(Synthetic example 3)

Polyoxyethylene (2.0)-2,2-bis(4-hydronalium KISHIFE nil)propane 64 weight section Isophthalic acid 16 weight section Terephthalic acid 16 weight section Maleic anhydride 0.6 weight section Dibutyltin oxide the raw material of 0.06 or more weight sections. It put into the 4 Thu mouth flask glass [ 2L ], and the thermometer, the stirring rod, and the nitrogen introducing pipe were attached, it decompressed one by one after a 24-hour reaction at 230 \*\* under the ordinary pressure nitrogen air current in the electric heat mantle heater, and the reaction was continued by 10mmHg. The reaction was pursued by the softening temperature according to ASTM-E 28-517, and when softening temperature amounted to 99 \*\*, it ended the reaction.

[0082]The obtained polymer (it expresses the resin C hereafter) is a colorless solid.

The acid value 7, the glass transition temperature of 62 \*\* by a DSC measurement method, and softening temperature were 101 \*\*.

[0083]

(Synthetic example 4)

Terephthalic acid 332 weight section Isophthalic acid . 332 weight sections Polyoxypropylene (2.2)-2,2-bis(4-hydronalium KISHIFE nil)propane 700 weight section Trimethylolpropane 80 weight section Ethylene glycol 75 weight section The tetrabutyl titanate 3 weight-section above-mentioned compound Stirrer, It puts into the 4 mouth flask which set the capacitor and



the thermometer, and it was made to react by ordinary pressure at 240 °C under a nitrogen gas air current for 10 hours, removing the water generated by dehydration condensation. It decompressed one by one after that, and the reaction was continued by 10mmHg. The reaction was pursued by softening temperature, and when softening temperature amounted to 151 °C, it ended the reaction. Tg according [ according to / in the softening temperature of the obtained polymer (it expresses the resin D hereafter) / 153 °C / acid value ] to 4 and a DSC measurement method was 65 °C.

[0084](Synthetic example 5)

Isophthalic acid 116 weight-section terephthalic acid 166 weight-section trimellitic anhydride 38 weight-section diethylene-glycol 26 weight-section neopentyl glycol 104 weight-section ethylene glycol 50 weight-section tetrabutyl titanate the raw material of 2.5 or more weight sections. It put into the 4 L round bottom flask glass [ 2L ], and the thermometer, the stirring rod, and the nitrogen introducing pipe were attached, it decompressed one by one after a 10-hour reaction at 240 °C under the ordinary pressure nitrogen air current in the electric heat mantle heater, and the reaction was continued by 10mmHg. The reaction was pursued by the softening temperature according to ASTM-E 28-517, and when softening temperature amounted to 148 °C, it ended the reaction. The obtained polymer (it expresses the resin E hereafter) is a colorless solid.

The acid value 4, the glass transition temperature of 72 °C by a DSC measurement method, and softening temperature were 151 °C.

[0085]T1/2 temperature measured using Shimadzu flow tester CFT-500 which is a constant stress extrusion type small tube type rheometer defines the softening temperature of resin. The measuring condition in the flow tester was performed on with piston cross-section area 1cm<sup>2</sup>, cylinder pressure 0.98MPa, die 1 mm in length, the diameter of a die hole of 1 mm, measurement start temperature 50°C, heating-rate °C/min of 6 degrees, and a sample weight of 1.5 g conditions.

[0086]

<The example of manufacture of a processing pigment> (processing pigment 1)

Organic color of resin A 650 weight section <formula 2> The raw material of 350 or more weight sections was kneaded with the two heating roll after mixing with the Henschel mixer. After-cooling coarse grinding was performed and the processing pigment 1 of 35% of pigment content was produced.

[0087](Processing pigment 2) The processing pigment 2 was produced completely like the case where the processing pigment 1 is produced, except using the resin A in production of the processing pigment 1 as the resin B.

[0088](Processing pigment 3) The processing pigment 3 was produced completely like the case where the processing pigment 1 is produced, except using the organic color of the formula 2 in production of the processing pigment 1 as the organic color of the formula 8.

[0089](Processing pigment 4) The processing pigment 4 was produced completely like the case where the processing pigment 1 is produced, except using the resin A in production of the processing pigment 1 as the resin E.

[0090](Processing pigment 1 for comparison) The processing pigment 1 for comparison was produced completely like the case where the processing pigment 1 is produced, except using the resin A in production of the processing pigment 1 as the resin C.

[0091](Processing pigment 2 for comparison) The processing pigment 2 for comparison was produced completely like the case where the processing pigment 1 is produced, except using the resin A in production of the processing pigment 1 as the resin D.

[0092](Processing pigment 3 for comparison) In the above-mentioned processing pigment 1, the processing pigment 3 for comparison was similarly obtained instead of the organic color of the formula 2 except having used the C.I. pigment red 122.

[0093](Processing pigment 4 for comparison) In the above-mentioned processing pigment 1, the processing pigment 4 for comparison was similarly obtained instead of the organic color of the

formula 2 except having used the C.I. pigment red 57:1.

[0094](Processing pigment 5 for comparison) In the above-mentioned processing pigment 4, the processing pigment 5 for comparison was similarly obtained instead of the organic color of the formula 2 except having used the C.I. pigment red 122.

[0095](Processing pigment 6 for comparison) In the above-mentioned processing pigment 4, the processing pigment 6 for comparison was similarly obtained instead of the organic color of the formula 2 except having used the C.I. pigment red 57:1.

[0096](Working example 1) Resin A93 weight section, paints (Carmine 190 (made by Arimoto chemicals company)) 4 weight section of the formula 2, Charge controlling agent (compound [ of the above <charge controlling agent 4> ], LR-147 (made by Japan Carlit Co., Ltd.)) 1 weight section, The amount part of carnauba wax (refining carnauba wax No.1, acid value 5, product made from SERARIKA NODA) duplexs was mixed with the Henschel mixer, melt kneading was carried out with the biaxial kneading machine, it pulverized and classified with the after-cooling jet mill, and the toner with a mean particle diameter of 8.0 micrometers was produced. [0097] Next, the magenta toner of working example 1 was obtained to this toner 100 weight section by carrying out externally adding of silica "NAX50" made from Japanese Aerosil 1 weight section, and the "RY-200" 1 weight section.

[0098]By similarly, carrying out melt kneading, grinding and classifying resin, an organic color (or processing pigment), a charge controlling agent, and WAX after cooling, with a biaxial kneading machine, by the presentation shown in Table 1, after fully mixing with a Henschel mixer, The toner of working example 2-8 and the comparative examples 1-5 was obtained by manufacturing a toner and also performing an externally adding process like working example 1.

[0099]

[Table 1]

表 1

	樹脂	着色剤	WAX	帯電制御剤	体積平均 ( $\mu\text{m}$ )
実施例 1	樹脂 A 9 3 部	式 2 の顔料 4 部	カナバ WAX 2 部	帯電制御剤 4 1 部	8.0
実施例 2	樹脂 A 8 5 部	加工顔料 1 1 2 部	カナバ WAX 2 部	帯電制御剤 4 1 部	7.8
実施例 3	樹脂 B 8 5 部	加工顔料 2 1 2 部	カナバ WAX 2 部	帯電制御剤 1 1 部	7.8
実施例 4	樹脂 A 8 5 部	加工顔料 3 1 2 部	カナバ WAX 2 部	帯電制御剤 4 1 部	7.8
実施例 5	樹脂 A 8 5 部	加工顔料 1 1 2 部	PPWAX 2 部	帯電制御剤 4 1 部	8.1
実施例 6	樹脂 A 8 5 部	加工顔料 1 1 2 部	カナバ WAX 2 部	E-84 1 部	8.0
実施例 7	樹脂 B 8 5 部	加工顔料 2 1 2 部	PETB 2 部	帯電制御剤 4 1 部	7.8
実施例 8	樹脂 A 8 5 部	加工顔料 3 1 2 部	PETB 2 部	帯電制御剤 4 1 部	8.0
比較例 1	樹脂 A 9 2 部	P.R. 122 5 部	カナバ WAX 2 部	帯電制御剤 4 1 部	7.8
比較例 2	樹脂 A 9 3 部	P.R. 57:1 4 部	カナバ WAX 2 部	帯電制御剤 4 1 部	7.9
比較例 3	樹脂 C 8 5 部	比較用加工顔料 1 1 2 部	カナバ WAX 2 部	帯電制御剤 4 1 部	7.9
比較例 4	樹脂 A 8 5 部	比較用加工顔料 3 1 2 部	カナバ WAX 2 部	帯電制御剤 4 1 部	7.9
比較例 5	樹脂 A 8 5 部	比較用加工顔料 4 1 2 部	カナバ WAX 2 部	帯電制御剤 4 1 部	8.0

[0100]The passage of the following [ cable address / in Table 1 ]. A part expresses a weight section.

— P.R.122;C.I. pigment red 122 (Fastogen Super Magenta R "Dainippon Ink & Chemicals, Inc. make")

— P.R.57:1;C.I. pigment red 57:1 (Symuler Brilliant Carmin six B285 "Dainippon Ink & Chemicals, Inc. make")

— PETB; — tetrabeheic acid ester carnauba wax [ of pentaerythritol ]; — refining carnauba wax No.1 (the acid value 5, product made from SERARIKA NODA)

- PPWAX; screw call 660P (polypropylene wax "Mitsuhiro transformation make")
- E-84; BONTORON E-84 (metal complex compound of salicylic acid "Orient chemicals company make")

[0101](Evaluation of the toner of Table 1) An exclusive toner is extracted from the cartridge of the printer (the "IPUSHIO color 2000" by Ricoh Co., Ltd.) of commercial one ingredient of nonmagnetic development system, The washed cartridge was filled up with the toner of working example and the comparative example which were shown in Table 1, and continuous printing of 10000 sheets was performed with 5% of image concentration. In order to evaluate the stability of the printing image to change of an environmental condition, the continuous printing examination was carried out under 25 \*\*, 50%, 32 \*\*, and 85% of two environment.

[0102](1) The image concentration and the greasing of image concentration, a greasing, and electrification quantity printed matter were measured by Macbeth densimeter RD-918. The greasing deducted and asked for the blank paper concentration before a print from the white part concentration after printing. \*\* and the time or more of 0.03 were made [ the time of the difference being less than 0.01 ] into x for O and the time of 0.01 to less than 0.03. The electrification quantity of the printing toner was measured using suction type small electrification quantity measuring device Mode210HS (made in Thorek).

[0103]A toner falls from the developing sleeve with which the cartridge was equipped after 10000 toner omission and toner scattering printing, or (2) (Toner omission), The state where \*\*, a lot of toner omissions, or toner scattering was accepted in the state where O, a little toner omissions, or toner scattering is accepted in the state where scatter around a developer and the inside of a machine (toner scattering) is not soiled was judged to be x.

[0104](3) Using the OHP transparency above-mentioned printer, the undecidedness arrival picture was formed on the OHP sheet, and the undecidedness arrival picture was established at 140 \*\* with the fixing unit used by the above-mentioned fixing / offset examination.

[0105]The OHP sheet created by the above procedure was projected on the white screen with the over head projector, and color definition was evaluated. Evaluation was performed visually, it was clear, and when it was the blackish projection image which has \*\* and muddiness in O and the case where transparency is a little missing and there is some muddiness if it is a transparent good projection picture, it was considered as x.

[0106]A result [ in / for the result in 25 \*\* and 50% / to Table 2 / 32 \*\* and 85% ] is shown in Table 3.

[0107]

[Table 2]

表 2					
	トナリ落ちトナリ飛散 初期 / 10000	画像濃度 初期 / 10000枚	地汚れ 初期 / 10000枚	帯電量 ( $\mu\text{C/g}$ )	OHP 透明性
実施例 1	O / Δ	1.39 / 1.42	O / O	-10.5	Δ
実施例 2	O / O	1.37 / 1.39	O / O	-12.0	O
実施例 3	O / O	1.39 / 1.42	O / O	-12.8	O
実施例 4	O / O	1.38 / 1.41	O / O	-12.7	O
実施例 5	O / O	1.36 / 1.39	O / O	-13.8	O
実施例 6	O / Δ	1.40 / 1.46	O / O	-10.0	O
実施例 7	O / O	1.36 / 1.37	O / O	-12.5	O
実施例 8	O / O	1.39 / 1.41	O / O	-12.5	O
比較例 1	Δ / x	1.33 / 1.59	O / Δ	-8.5	x
比較例 2	O / x	1.38 / 1.48	Δ / x	-9.2	Δ
比較例 3	O / O	1.38 / 1.41	O / O	-12.3	O
比較例 4	O / Δ	1.33 / 1.45	O / Δ	-9.8	O
比較例 5	O / Δ	1.33 / 1.45	O / Δ	-9.7	O

[0108]

[Table 3]

表3

	トナー落ち・トナー飛散 初期/10000枚	画像濃度 初期/10000枚	地汚れ 初期/10000枚	帯電量 ( $\mu\text{C/g}$ )	OHP 透明性
実施例1	○/△	1.36/1.30	○/○	-9.5	△
実施例2	○/○	1.34/1.30	○/○	-11.1	○
実施例3	○/○	1.36/1.31	○/○	-12.3	○
実施例4	○/○	1.35/1.31	○/○	-12.0	○
実施例5	○/○	1.33/1.28	○/○	-12.5	○
実施例6	○/△	1.38/1.44	○/○	-8.9	○
実施例7	○/○	1.33/1.30	○/○	-11.6	○
実施例8	○/○	1.37/1.33	○/○	-12.2	○
比較例1	△/×	1.28/1.22	○/×	-7.7	×
比較例2	○/×	1.32/1.10	△/×	-5.1	△
比較例3	○/△	1.35/1.25	○/△	-12.2	○
比較例4	○/×	1.28/1.16	○/×	-8.1	○
比較例5	○/×	1.27/1.16	○/×	-8.1	○

[0109](4) The non-fixed image sample of A-4 paper size is produced with the test machine which converted the printer of one ingredient of nonmagnetic development system of fixing/offset test marketing by heat roll fixing. Fixing starting temperature and the existence of the offset phenomenon were checked in the following test condition using the heat roll fixing unit of the following specification.

ロール材質           上：四弗化エチレン  
                           下：HTVシリコーン  
 ロール形状           径：50mm  
                           長さ：370mm  
 上ロール荷重        ： 7kg  
 上/下ロールニップ幅   ： 4mm  
 紙送り速度          ： 100mm/sec

In order to measure fixing starting temperature, it asked for the image concentration residual ratio calculated by the following formula.

[0110]Image concentration residual ratio = after [ a fastness test ] image concentration / said left examination previous image concentration \* image concentration was measured in Macbeth image concentration meter RD-918.

\* The image concentration after a fastness test is the image concentration after grinding a fixed image using a Gakushin-type fastness-to-rubbing testing machine (load: 200 g, grinding operation:5 stroke).

It was considered as the level which is satisfactory practically by not less than 80% of the image concentration residual ratio, and the minimum temperature was made into fixing starting temperature.

[0111]Offset starting temperature observed the fixed image sample, and made it the temperature an offset phenomenon is visually accepted to be. The result was shown in Table 4.

[0112]

[Table 4]

表4

	定着開始温度／オフセット開始温度 ℃
実施例1	130-210
実施例2	130-210
実施例3	125-210
実施例4	130-210
実施例5	140-210
実施例6	130-210
実施例7	125-210
実施例8	130-210
比較例1	130-210
比較例2	130-210
比較例3	140-210
比較例4	130-210
比較例5	130-210

[0113](Working example 9) Resin E85 weight section and the processing pigment 4 as 12 weight sections and a charge controlling agent TP-415(product made from Hodogaya chemicals)1 weight section of quarternary-ammonium-salt structure, The amount part of carnauba wax (refining carnauba wax No.1, acid value 5, product made from SERARIKA NODA) duplex was mixed with the Henschel mixer, melt kneading was carried out with the biaxial kneading machine, it pulverized and classified with the after-cooling jet mill, and the toner with a mean particle diameter of 8.0 micrometers was produced.

[0114]Next, the positive triboelectric charging magenta toner of working example 9 was obtained to this toner 100 weight section by carrying out externally adding of the silica "TG820F" made from Cabot Specialty Chemicals ink1 weight section. Subsequently, this toner 5 weight section and ferrite carrier 95 weight section with a mean particle diameter of 80 micrometers which covered silicone resin were mixed with the ball mill, and it was considered as the two component developer.

[0115]By similarly, carrying out melt kneading, grinding and classifying resin, an organic color (or processing pigment), a charge controlling agent, and WAX after cooling, with a biaxial kneading machine, by the presentation shown in Table 5, after fully mixing with a Henschel mixer, The toner of the comparative examples 6-8 was obtained by manufacturing a toner and also performing an externally adding process like working example 9.

[0116]

[Table 5]

表5

	樹脂	着色剤	WAX	帯電制御剤	体積平均径 ( $\mu$ m)
実施例 9	樹脂E 85部	加工顔料4 12部	加ハ WAX 2部	TP-415 1部	8.0
比較例 6	樹脂D 85部	比較用加工顔料2 12部	加ハ WAX 2部	TP-415 1部	7.8
比較例 7	樹脂E 85部	比較用加工顔料5 12部	加ハ WAX 2部	TP-415 1部	7.9
比較例 8	樹脂E 85部	比較用加工顔料6 12部	加ハ WAX 2部	TP-415 1部	7.9

[0117](Evaluation of the toner of Table 5)

[0118](1) Using a commercial laser beam printer (selenium photo conductor loading) by the two component developer of the printing torture test table 5 under 25 \*\*, 50% and 32 \*\*, and 85% of conditions, Performed printing of 50000 sheets, and the concentration and greasing concentration of the picture part before and behind a continuous print were measured, and the electrification quantity of the developer was measured. Image concentration and a greasing were measured by Macbeth densimeter RD-918. The greasing deducted and asked for the blank paper concentration before a print from the white part concentration after printing. \*\* and the time or more of 0.03 were made [ the time of the difference being less than 0.01 ] into x for O and the

time of 0.01 to less than 0.03.

[0119] Visual observation of the scattering situation of the toner inside the development counter after 50000-sheet printing was carried out. Although O and scattering could hardly be seen in the state where scattering is not observed at all, when the inside of a device was wiped with the waste cloth, the state where x and severe scattering inside the plane could check the state where \*\* and scattering inside the plane can check visually the state where toner soiling is observed was made into xx.

[0120] About electrification quantity, the toner was extracted from the inside of a developer and it measured with blowing off electrification quantity measuring apparatus (made by Toshiba Chemical).

[0121] A result [ in / for the result in 25 \*\* and 50% / to Table 6 / 32 \*\* and 85% ] is shown in Table 7.

[0122]

[Table 6]

表 6

	画像濃度 初期／50000枚	地汚れ 初期／50000枚	帯電量 ( $\mu\text{C}/\text{g}$ )	トナーの飛散状況
実施例 9	1.33／1.36	○／○	18.5	○
比較例 6	1.32／1.38	○／○	16.8	○
比較例 7	1.36／1.47	○／△	20.5	×
比較例 8	1.35／1.46	○／△	16.5	×

[0123]

[Table 7]

表 7

	画像濃度 初期／50000枚	地汚れ 初期／50000枚	帯電量 ( $\mu\text{C}/\text{g}$ )	トナーの飛散状況
実施例 9	1.38／1.40	○／○	17.8	○
比較例 6	1.35／1.43	○／△	14.8	△
比較例 7	1.38／1.49	○／×	19.6	×
比較例 8	1.37／1.47	○／×	15.8	×

[0124](2) The non-fixed image sample was produced using the method of fixing/offset test above by heat roll fixing, and fixing starting temperature and offset starting temperature were investigated using the same heat roll fixing unit as the first half. A test result is shown in Table 8.

[0125]

[Table 8]

表 8

	定着開始温度／オフセット開始温度 ℃
実施例	140-220
比較例	150-220
比較例	140-220
比較例	140-220

[0126]

[Effect of the Invention] The color toner for electrostatic charge image development of this invention shows the stable electrifying characteristic, even if it has the outstanding tinting strength and hue and changes environment, such as temperature and humidity. So, it excels in color reproduction nature, electrification quantity is not changed, but good and stable printing image quality is shown. Good fixability is shown also on a low energy fixing condition like low temperature fixation or short-time fixing, and it excels also in offset-proof nature.

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TECHNICAL FIELD

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[Field of the Invention]This invention relates to color toner for electrostatic charge image development for developing the electrostatic charge image in electro photography, electrostatic recording, electrostatic printing, etc., and a manufacturing method for the same.

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[Translation done.]

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PRIOR ART

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[Description of the Prior Art]As a toner composition for obtaining a visible image by a xerography, many things which many made distribute black colorant like carbon black in binder resin are used. However, these days, the color toner which distributed cyanogen paints, a magenta pigment, a yellow pigment, or other chromatic color paints in the binder is also used, and the copying machine of full color or a mono color and printer using these color toner are developed.



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EFFECT OF THE INVENTION

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[Effect of the Invention]The color toner for electrostatic charge image development of this invention shows the stable electrifying characteristic, even if it has the outstanding tinting strength and hue and changes environment, such as temperature and humidity. So, it excels in color reproduction nature, electrification quantity is not changed, but good and stable printing image quality is shown. Good fixability is shown also on a low energy fixing condition like low temperature fixation or short-time fixing, and it excels also in offset-proof nature.

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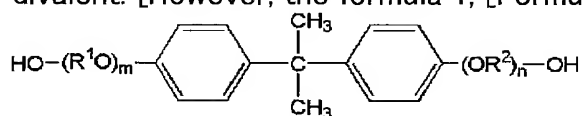
1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.\*\*\*\* shows the word which can not be translated.

3.In the drawings, any words are not translated.

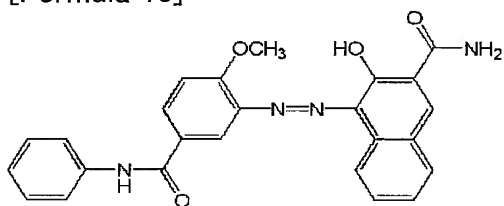
## MEANS

[Means for Solving the Problem]This invention persons came to complete this invention, as a result of repeating research wholeheartedly that above-mentioned SUBJECT should be solved. Namely, in color toner for electrostatic charge image development in which this invention contains binder resin and colorant, Said binder resin is the main ingredients about one or more sorts of polybasic acid compounds chosen from a group which consists of polybasic acid, acid anhydrides, and these lower alkyl ester more than (A) divalent, and fatty alcohol more than (B) divalent. [However, the formula 1, [Formula 9]



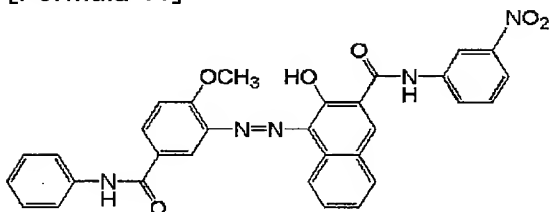
(Formula 1)

(among a formula,  $\text{R}^1$  and  $\text{R}^2$  are the same or different, ethylene or a propylene group is shown, m and n are the same or different, and the integer of 0-7 is shown, and  $m+n$  shows the integer of 0-7.) —] except the compound which has a bisphenol skeleton expressed The polyester resin which carries out, and is produced by making react is contained, and said colorant is the formula 2, the formula 3, the formula 4, the formula 5, the formula 6, the formula 7, and the formula 8, [Formula 10]



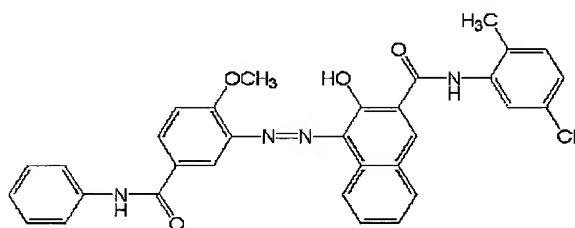
(Formula 2)

[Formula 11]

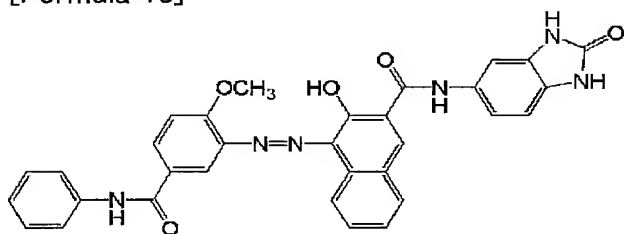


(Formula 3)

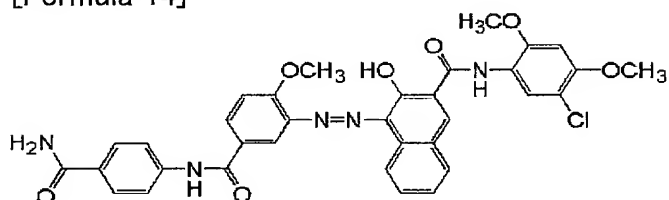
[Formula 12]



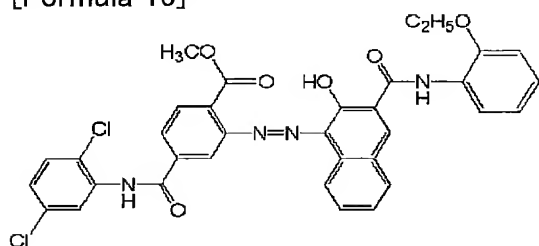
(Formula 4)  
[Formula 13]



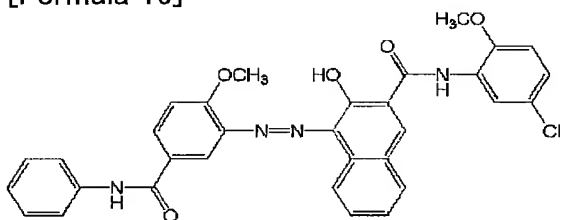
(Formula 5)  
[Formula 14]



(Formula 6)  
[Formula 15]



(Formula 7)  
[Formula 16]



(Formula 8)

The color toner for electrostatic charge image development being one sort or the organic color beyond it chosen from \*\* is provided.

[0012] Said some of binder resin is used for this invention for one sort or the organic color beyond it chosen from said formula 2, the formula 3, the formula 4, the formula 5, the formula 6, the formula 7, and the formula 8, After performing distributed processing beforehand, the manufacturing method of the color toner which carries out diluent powder using said binder resin further is provided.

[0013]

[Embodiment of the Invention] Hereafter, this invention is explained in detail. The binder resin used for the color toner for electrostatic charge image development of this invention is polyester resin.

[0014] As a polybasic acid compound (A) chosen from the polybasic acid, the acid anhydrides, and/or these lower alkyl ester more than divalent for manufacturing the polyester resin used by this invention, For example, phthalic anhydride, terephthalic acid, isophthalic acid, orthophthalic acid, Naphthalene dicarboxylic acid, adipic acid, maleic acid, a maleic anhydride, Fumaric acid, itaconic acid, citraconic acid, hexahydro phthalic anhydride, Tetrahydro phthalic anhydride, cyclohexanedicarboxylic acid, succinic acid, Dicarboxylic acid, such as malonic acid, glutaric acid, azelaic acid, and sebacic acid, the derivative of those, or its esterification material, Polyvalent carboxylic acid of three or more organic functions, such as trimellitic acid, trimellitic anhydride, pyromellitic acid, and pyromellitic dianhydride, the derivative of those, or its esterification material is mentioned, for example.

[0015] As fatty alcohol (B) more than divalent, For example, 1,4-cyclohexane dimethanol, ethylene glycol, A diethylene glycol, triethylene glycol, propylene glycol, Dipropylene glycol, tripropylene glycol, butanediol, Pentanediol, hexandiol, a polyethylene glycol, a polypropylene glycol, Ethylene oxide propylene oxide random copolymer diol, Ethylene oxide propylene oxide block copolymer diol, Diol, such as ethylene oxide tetrahydro franc copolymer diol and poly KAPUOKAKU ton diol, Sorbitol, 1,2,3,6-hexanetetraol, 1, 4-sorbitan, Pentaerythritol, 1,2,4-butanetriol, 1 and 2, 5-pentanetriol, Polyhydric alcohol of three or more organic functions, such as glycerin, isobutane triol, 2-methyl-1,2,4-butanetriol, trimethylolethane, trimethylolpropane, and 1,3,5-TORIMECHI roll benzene, is mentioned.

[0016] The compound which has two or more glycidyl groups can also be used into one molecule as fatty alcohol (B) more than divalent [ reacted to the carboxylic acid compound of the above (A) ]. Specifically, there are neopentyl glycol diglycidyl ether, glycerol triglycidyl ether, trimethylolpropane triglycidyl ether, trimethylolethane triglycidyl ether, pentaerythritol tetraglycidyl ether, etc., for example.

[0017] In this invention, aromaticdiol or polyhydric alcohol more than trivalent can also be used together in the range which does not affect performance. As aromaticdiol or polyhydric alcohol more than trivalent, For example, catechol, resorcinol, hydroquinone, a bisphenol A type epoxy resin, bisphenol F type epoxy resin, a bisphenol smooth S form epoxy resin, cresol novolak type epoxy resin, phenol novolak type epoxy resin, etc. are mentioned. However, the compound which has a bisphenol A skeleton expressed with the above-mentioned formula 1 is removed. As aromaticdiol removed, for example Bisphenol A, polyoxyethylene (2.2)-2,2-bis(4-hydroxyphenyl) propane, Polyoxyethylene (2.0)-2,2-bis(4-hydroxyphenyl)propane, Polyoxypropylene (2.0)-2,2-bis(4-hydroxyphenyl)propane, Polyoxypropylene (2.2)-polyoxyethylene (2.0)-2,2-bis(4-hydroxyphenyl)propane, Polyoxypropylene (6)-2,2-bis(4-hydroxyphenyl)propane, Polyoxypropylene (2.2)-2,2-bis(4-hydroxyphenyl)propane, Polyoxypropylene (2.4)-2,2-bis(4-hydroxyphenyl)propane, polyoxypropylene (3.3)-2,2-bis(4-hydroxyphenyl)propane, these derivatives, etc. are mentioned.

[0018] By using fatty alcohol more than divalent in this invention, the chain of polyester resin becomes flexible, When it mixes with a carrier and the toner using such polyester resin is used as a two component developer, there is an effect which eases the stress which a carrier receives within a developer, it prevents the resin coating phase of a carrier surface exfoliating, and the effect that the life of a developer is prolonged as a result is acquired. The share received when it uses as a toner for one ingredient of nonmagnetic development and a toner passes through between a developing sleeve and charge members can be eased, and it can be considered as a high durability developer.

[0019] When a polyester main chain elasticity-izes, the fixability in low temperature is improved. Although adding a wax in a toner is a means generally used, in order to improve fixing / offset performance, Especially in polyester resin using fatty alcohol more than divalent [ in this invention ], the compatibility of waxes is good and the fixing performance and offset-proof nature in low temperature are improved further.

[0020]Therefore, it is necessary to use the above-mentioned aromaticdiol in the range which does not spoil the main point of this invention. As for the quantity using the above-mentioned aromaticdiol, it is desirable that it is less than 30 mol % to all the alcohol components. It is less than 20 mol % more preferably.

[0021]As carboxylic acid components used by this invention, dimethyl naphthalate, diethyl naphthalate, dibutyl naphthalate, etc. are more suitably used as naphthalene dicarboxylic acid and/or its lower alkyl ester. These compounds need to use more than 1 mol % of a total acid component, and are more than 5 mol % more preferably.

[0022]A monomer including naphthalene ring structure has an effect in raising Tg of resin, and its heat-resistant cohesiveness of resin improves. In the system which used elastic fatty alcohol for the subject especially as an alcohol component, the fall of Tg of resin can be suppressed and resin having both the low temperature fixability by using fatty alcohol more than divalent and the heat-resistant cohesiveness by naphthalene dicarboxylic acid can be obtained.

[0023]Polyester resin in this invention can be obtained by performing a dehydrating condensation reaction or an ester exchange reaction using the above-mentioned raw material component (A) and (B), for example under existence of a catalyst. Although in particular the reaction temperature and reaction time in this case are not limited, they are usually 2 to 24 hours at 150-300 °C.

[0024]Composition of such polyester resin can also be performed by adding a catalyst. As an esterification catalyst to be used, the organic metal like dibutyltin dilaurate and dibutyl tin oxide, the metal alkoxide like tetrabutyl titanate, etc. are mentioned, for example. A transesterification catalyst can be used when the carboxylic acid components to be used are lower alkyl ester. As a transesterification catalyst, zinc acetate, lead acetate, metal acetate like magnesium acetate or a zinc oxide, the metallic oxide like antimony oxide, or the metal alkoxide like tetrabutyl titanate is mentioned, for example. About the addition of a catalyst, it is preferred to consider it as 0.01 to 1% of the weight of the range to the total amount of raw material.

[0025]Although the glass transition temperature (Tg) of the polyester resin used for this invention has a not less than 50 °C preferred thing, the Tg of especially a not less than 55 °C thing is preferred especially. Below 50 °C, Tg tends to produce blocking high (heat condensation), when a toner is exposed under an elevated temperature inside preservation, conveyance, or the developer of a machine.

[0026]as softening temperature of the polyester resin used for this invention, the thing of the range of 90 °C - 180 °C is preferred also in not less than 90 °C -- it is the range of 95 °C - 160 °C more preferably. When softening temperature is less than 90 °C, a toner tends to produce isoagglutination and it is easy to become a trouble in the time of preservation, or the case of printing, and in exceeding 180 °C, fixability worsens in many cases.

[0027]when the transparency at the time of making it especially established on the color reproduction nature at the time of a color pile or an OHP sheet is required as full color toner, as softening temperature of polyester resin, the thing of the range of 90 °C - 130 °C is preferred -- it is the range of 95 °C - 120 °C more preferably.

[0028]As acid value of polyester resin of this invention, it is preferred that they are 20 or less mgKOH/g at the point that the moisture resistance of a toner becomes good.

[0029]T1/2 temperature measured using Shimadzu flow tester CFT-500 which is a constant stress extrusion type small tube type rheometer defines the softening temperature of resin in this invention. The measuring condition in the flow tester was performed on with piston cross-section area <sup>2</sup> of 1 cm, cylinder pressure 0.98MPa, die 1 mm in length, the diameter of a die hole of 1 mm, measurement start temperature 50°C, heating-rate C/min of 6 degrees, and a sample weight of 1.5 g conditions.

[0030]Although it is used in this invention out of the organic color expressed with said formula 2, the formula 3, the formula 4, the formula 5, the formula 6, the formula 7, and the formula 8, choosing one sort or more than it, The magenta pigment usually used with the conventional toner by using these paints, For example, the color toner which has good tinting strength, story tonality, definition, and transfer property as compared with the C.I.Pigment Red 122 grade which

are C.I.Pigment Red 57:1 and a quinacridone pigment can be obtained. When continuous printing is carried out, a stable electrification behavior can be shown, and the high-definition picture excellent in color reproduction nature and transparency can be printed.

[0031]The Color Index number of the above-mentioned organic color is as follows.

The organic color of the formula 2; C.I.Pigment. The organic color of the Red 150 formula 3; C.I.Pigment. The organic color of the Red 31 formula 4; C.I.Pigment. The organic color of the Red 147 formula 5; C.I.Pigment. organic color [ of the Red 176 formula 6 ]; -- organic color [ of the C.I.Pigment Red 187 formula 7 ]; -- organic color [ of the C.I.Pigment Red 188 formula 8 ]; -- in C.I.Pigment Red 269 this invention, It is preferred to use the organic color expressed with the formula 2 and/or the formula 8 also in the above. It is more preferred to use the organic color expressed with the formula 2.

[0032]The amount of the organic color used expressed with the formula 2 in this invention, the formula 3, the formula 4, the formula 5, the formula 6, the formula 7, and the formula 8 has the preferred range of one to 50 weight section per binder resin 100 weight section, its range of two to 30 weight section is more preferred, and especially its range of two to 20 weight section is preferred.

[0033]In addition to the above-mentioned organic color, in the range which does not lose the effect of this invention, since hue is adjusted, others and colorant can be added and used in this invention. As such colorant, although a well-known thing is raised, For example, as colorant of a blue system the C.I.Pigment Blue 60 grade of C.I.Pigment Blue 15-3 of a phthalocyanine system and an indanthrone system, As reddish colorant. C.I.Pigment of a \*\* quinacridone series. Red 122 and azo C.I.Pigment. Red 22, C.I.Pigment Red23, C.I.Pigment Red31, C.I.Pigment Red48:1, C.I.Pigment Red 48:3, and C.I.Pigment Red 57:1 grade as colorant of a yellow system. C.I.Pigment Yellow12 of \*\* azo, C.I.Pigment Yellow 13, C.I.PigmentYellow 14, C.I.Pigment Yellow 17, and C.I.Pigment. There are Yellow 97, C.I.Pigment Yellow 155, C.I.Pigment Yellow151 of a benzimidazolone system, C.I.Pigment Yellow 154, C.I.Pigment Yellow 180, etc.

[0034]The above quoted paints can be used together with the organic color of the formula 2 - the formula 8 in the range which does not spoil the purpose of this invention. For example, by combining with yellow system paints, it can also be made the toner of a LGT color system and can also be considered as the toner of a blue-purple color system by combining with cyan color system paints. The magenta toner which has a clear magenta color with tinting strength can be obtained by using together with the red pigment of the blueness of C.I.Pigment Red 122, C.I.Pigment Red 23, and C.I.Pigment Red31 grade especially.

[0035]When using together the paints of the formula 2 - the formula 8, and other paints, as for the amount of the paints used of the formula 2 - the formula 8, 40 % of the weight or more is preferred to the content of the whole paints, and it is 50 % of the weight or more more preferably.

[0036]Although publicly known various waxes, for example, polypropylene wax, polyethylene wax, a polyamide system wax, the Fischer Tropsch wax, etc. can be suitably used for the toner of this invention as a release agent until now, It is preferred to use the wax which contains a higher fatty acid ester compound and/or an aliphatic alcohol compound especially as a release agent.

[0037]Also in the wax containing a higher fatty acid ester compound and/or an aliphatic alcohol compound, natural wax, such as carnauba wax, a montan ester wax, a rice wax, and a scale insect wax, and/or especially a synthetic ester system wax are preferred. Especially as a synthetic ester system wax, tetrabehenic acid ester of pentaerythritol is preferred.

[0038]These waxes show good dispersibility to especially polyester resin, and their improvement of fixability and offset-proof nature is remarkable. these waxes -- many -- also in several sheets and prolonged printing, For example, without adhering to the charge members forced on the developing sleeve, when it uses as a toner for one ingredient of nonmagnetic development, electrification stable in the toner is given, there is neither an image defect nor a greasing, and printing of a high-definition and high definition picture is attained. When it uses with one sort or the organic color beyond it chosen from said formula 2 used by this invention - the formula 8 and is considered as color toner, the color toner which was excellent in transparency as compared with the wax of a hydrocarbon system like polypropylene wax is obtained. The color

toner which has such the characteristic is transparent, and fits printing to the OHP sheet in which a skillful projection picture is called for, and the use which prints two or more colors in piles, and prints the neutral colors of good color reproduction nature.

[0039]It is preferred to use the de-free fatty acid carnauba wax which removed free fatty acid by refining as carnauba wax. As acid value of de-free fatty acid carnauba wax, three or less are preferred and it is two or less acid value more preferably. From conventional carnauba wax, de-free fatty acid carnauba wax serves as micro crystallite, and its dispersibility in the inside of polyester resin improves. A montan ester wax is refined from a mineral, and serves as micro crystallite like carnauba wax by refining, and its dispersibility in the inside of polyester resin improves. It is preferred that it is 30 or less as acid value especially in a montan ester wax. A rice wax refines a rice bran low and, as for acid value, it is preferred that it is 13 or less. the wax in which the larva of a scale insect (alias IBOTAROU MUSHI) secretes a scale insect wax -- it can obtain by melting the \*\* ingredient in boiling water, for example, and carrying out after-separation cooling solidification of the upper layer, or repeating it. The scale insect wax refined by such a means is white in a solid state, shows the very sharp melting point, and is suitable as a wax for toners in this invention. Acid value becomes ten or less by refining, and five or less are preferred as an object for toners.

[0040]The above-mentioned wax may be used independently, or it may combine, it may be used, and good fixing offset performance is obtained by carrying out 1-30 weight-section content preferably 0.3 to 40 weight section to binder resin. It is one to 20 weight section more preferably. If less than 0.3 weight sections, offset-proof nature will be spoiled, and if more than 40 weight sections, the mobility of a toner will worsen. By adhering to a carrier surface in a two-ingredient development system, it is generated by the SUPENTO career, and it will have an adverse effect on the electrifying characteristic of a toner, or will adhere to the layer thickness regulating member welded by pressure to the developing roll in one ingredient of nonmagnetic development system.

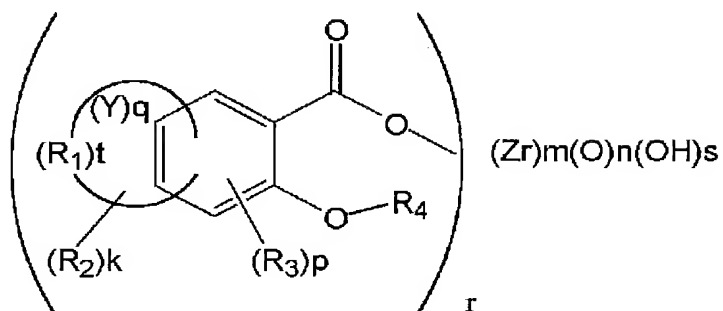
[0041]In this invention, a charge controlling agent can be used if needed. As a right charge controlling agent, for example, a nigrosine series color, triphenylmethane dye, Resin containing quarternary ammonium salt, the 4th class ammonium, and/or an amino group, etc., As a negative electrification controlling agent, a trimethyl ethane system color, the metallic complex of salicylic acid, The metallic complex of benzoic acid, a copper phthalocyanine, perylene, Quinacridone, There are resin containing heavy metal content acid dye, such as azo pigment, metallic complex azo dye, and an azochromium complex, a calyx allene type phenol system condensate, an annular polysaccharide, a carboxyl group, and/or a sulfonyl group, etc.

[0042]It is desirable to use a colorless charge controlling agent in this invention especially, As a negative charge controlling agent, as a metal complex compound of salicylic acid, "BONTORON E-84" by an Orient chemicals company. "TN105" by the Hodogaya chemicals company and "N4PVP-2481" by Clariant, LTD. etc. As a colorless right charge controlling agent, TP-302 of quarternary-ammonium-salt structure, TP-415, TP-610; (product made from the Hodogaya chemicals), BONTORON P-51; (product made from Orient chemicals), the copy charge PSY (Clariant Japan), etc. are used suitably. "FCA-201-PS" (FUJIKURA KASEI CO., LTD.) etc. is mentioned as a positive triboelectric charging resin mold charge controlling agent containing the 4th class ammonium and/or an amino group.

[0043]Especially, as a charge controlling agent which can be especially used conveniently in this invention, there are a compound of the following formula 9 and a compound of the formula 10.

<Formula 9> [0044]

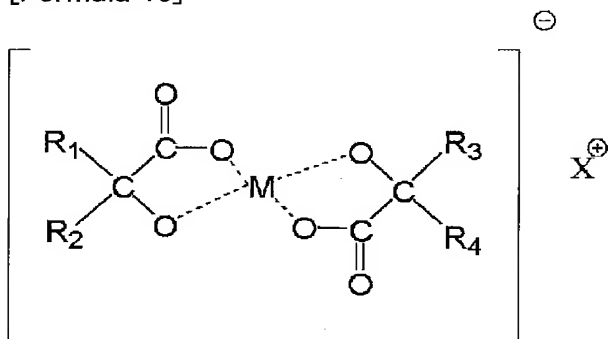
[Formula 17]



$R_1$  is the 4th class carbon, methine, and methylene among a formula -- N and S. The hetero atom of O and P may be included and Y expresses the cyclic structure connected with the saturated bond or the unsaturated bond, Mutually  $R_2$  and  $R_3$  independently An alkyl group, an alkenyl group, The aryl group, aryloxy group or aralkyl group which may have an alkoxy group and a substituent, or an aralkyloxy group, The amino group, carboxyl group which may have a halogen group, hydrogen, a hydroxyl group, and a substituent, A carbonyl group, a nitro group, a nitroso group, a sulfonyl group, and a cyano group are expressed,  $R_4$  expresses hydrogen or an alkyl group and t 0 thru/or the integer of 1-12, m -- as for the integer of 0 thru/or 1-4, and q, the integer of 0 thru/or 1-20 and k are [ the integer of 1 to 20, and n / the integer of 0 thru/or 1-4, and p / the integer of 1 to 20 and s of the integer of 0 thru/or 1-3 and r ] the integers of 0, or 1 thru/or 20.

[0045]<Formula 10> [0046]

[Formula 18]

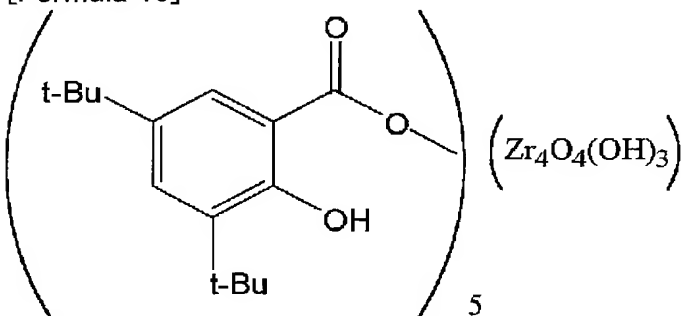


the inside of a formula,  $R_1$ , and  $R_4$  -- a hydrogen atom and an alkyl group. Substitution or an unsubstituted aromatic ring (a condensed ring is also included) is shown,  $R_2$  and  $R_3$  show substitution or an unsubstituted aromatic ring (a condensed ring is also included), M shows one sort of trivalent metal chosen from B, aluminum, Fe, Ti, Co, and Cr, and  $X^+$  shows a cation.

[0047]As a concrete example of the compound of <the formula 9>, there is following < charge controlling agent 1>- <charge controlling agent 3>.

[0048]<Charge controlling agent 1> [0049]

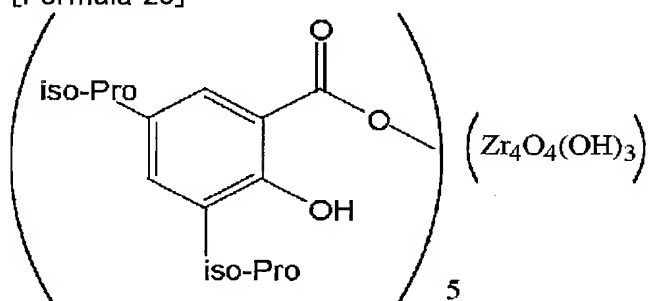
[Formula 19]





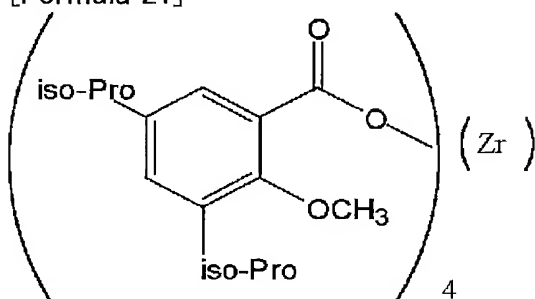
[0050]&lt;Charge controlling agent 2&gt; [0051]

[Formula 20]



[0052]&lt;Charge controlling agent 3&gt; [0053]

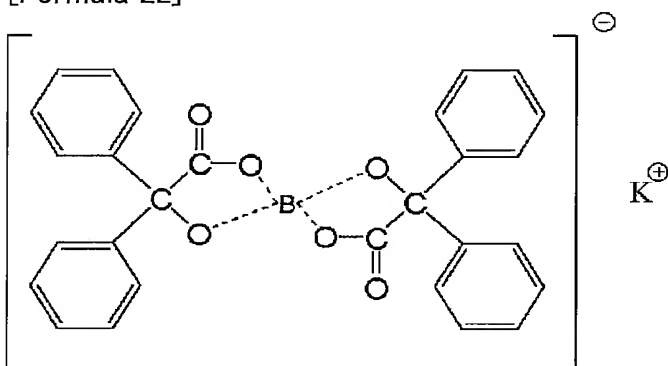
[Formula 21]



[0054]As a concrete example of the compound of <the formula 10>, there are the following <charge controlling agents 4> and the <charge controlling agent 5>.

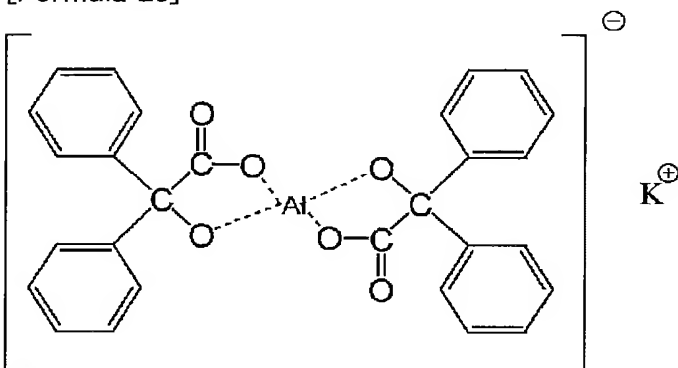
[0055]&lt;Charge controlling agent 4&gt; [0056]

[Formula 22]



[0057]&lt;Charge controlling agent 5&gt; [0058]

[Formula 23]



[0059]The above-mentioned charge controlling agent may be used independently, or it may

combine, it may be used, and good electrification performances are obtained by carrying out 0.5–5 weight–section content preferably 0.3 to 15 weight section to binder resin.

[0060]Although it can therefore obtain for arbitrary means of publicly known common use, after carrying out melt kneading of a wax and the various additive agents, for example to resin and colorant if needed above the melting point (softening temperature) of resin, a manufacturing method for obtaining a toner of this invention can be ground, and can be obtained by classifying. in order to make an effect of this invention reveal further, it is good to distribute some binder resin which uses one sort or an organic color beyond it chosen from said formula 2 – the formula 8 at high concentration, and to carry out diluent powder to binder resin which uses this dispersed matter after that.

[0061]Thus, as a process which makes binder resin distribute colorant beforehand at high concentration, a publicly known method, i.e., the masterbatch method, a flushing process, etc., can be used conventionally. The masterbatch method is a method of obtaining a good dispersed matter, by kneading colorant with resin at high concentration using a kneader or a roll mill, applying a high share. A flushing process is a method of obtaining a dispersed matter of high pigment concentration, carrying out heat kneading of a hydrous paste and binder resin of paints with a pressurized kneader, replacing water and binder resin, and removing moisture.

[0062]As for a rate of binder resin in this dispersed matter of high pigment concentration, and colorant, it is preferred that the amount of coloring matters is in ten weight sections – 100 weight sections to binder resin 100 weight section.

[0063]It mixes by a kneading means of 2 rolls, 3 rolls, a pressurized kneader, or a biaxial extruder by using concrete for example, above–mentioned resin and colorant as an essential ingredient. Under the present circumstances, although colorant should just distribute uniformly in resin and conditions in particular of that melt kneading are not limited, they are usually 10 minutes – 2 hours at 80–180 \*\*.

[0064]Coarse grinding aiming at mitigation of load in a pulverizing process and improvement in the efficiency of comminution is performed if needed. Although in particular a device and conditions that are used for coarse grinding are not limited, it is common to carry out coarse grinding to particle diameter below a 3–mm mesh pass with ROTOPU REXX, a PARUPE riser, etc.

[0065]Subsequently, it pulverizes with air type grinders, such as mechanical grinders, such as a turbo mill and KURIPU TRON, a whorl type jet mill counter jet mill, and a collision plate type jet mill, and a method of classifying with a pneumatic elutriation machine etc. is mentioned. What is necessary is to choose and just to set up pulverizing and a device of a classification, and conditions become desired particle diameter, particle size distribution, and particle shape.

[0066]In this invention, various additive agents (it is called an external additive) can be used for surface treatment of toners, such as fluid improvement in a toner, and electrifying characteristic improvement. As an external additive which can be used by this invention, For example, a silicon dioxide, titanium oxide, oxidation aluminum, cerium oxide, a zinc oxide, Non–subtlety granular materials, such as tin oxide and zirconium oxide, and them Silicone oil, What carried out the surface treatment by hydrophobing processing agents, such as a silane coupling agent, polystyrene, Resin pulverized coal, such as an acrylic, a styrene acrylic, polyester, polyolefine, cellulose, polyurethane, benzoguanamine, melamine, nylon, silicone, phenol, and vinylidene fluoride, etc. are used.

[0067]A silicon dioxide (silica) which carried out hydrophobing processing of the surface by various kinds of polyorganosiloxanes and hexamethylenedisilazane, a silane coupling agent, etc. also in these can use conveniently especially. There are some which are marketed with the following trade names as such a thing, for example.

[0068]AEROSIL R972, R974, R202, R805, R812, RX200, RY200, R809, RX50, RA200HS, RA200H [Japanese Aerosil, Inc.]

WACKER HDK H2000, H1018, H2050EP, HDKH3050EP, HVK2150 [Wacker Chemicals yeast AJIA, Inc.]

Nipsil SS–10, SS–15, SS–20, SS–50, SS–60, SS–100, SS–50B, SS–50F, SS–10F, SS–40, SS–70, SS–72F, [Japanese Silica Industry]

CABOSIL TG820F, TS-530, TS-720 [Cabot Specialty Chemicals ink]

[0069]Particle diameter of an external additive is 1/10 or less desirable especially suitably [ that it is 1/3 or less / of a diameter of a toner ]. These external additives may use together two or more sorts of different mean particle diameter.

[0070]By using together a thing of particle diameter size, and a thing of particle diameter smallness in a toner for one ingredient of nonmagnetic development especially, toner flow kinesis and development durability are raised, the long-term stability of adherence to a braid of a developing machine and prevention of fogging, and electrification at the time of running, etc. are acquired, and it is desirable.

[0071]A using rate of an external additive is 0.1 to 3 % of the weight preferably 0.05 to 5% of the weight to matrix toner 100 weight section.

[0072]Said silica can be performed to particle toner as a method of carrying out externally adding, for example using a Henschel mixer etc. which are the usual mixers for granular materials, and what is called surface treatment machines, such as a hybridizer. It may be made for silica to make this externally adding process adhere on the surface of particle toner, and a part of silica may be made to be embedded at particle toner.

[0073]Color toner for electrostatic charge image development of this invention can be used as an object for the development of an electrostatic latent image by a xerography as a two component developer mixed with the one-ingredient developer, one ingredient of nonmagnetic developer, or a career. There is no restriction in particular in a kind of career, and a career which carried out the resin coat to iron powder of publicly known common use, a ferrite, magnetite, etc. and them is used.

[0074]Although the core agent of a career can use iron powder used for the usual two-ingredient development system, magnetite, a ferrite, etc., since true specific gravity is low, high resistance, and is excellent in environmental stability and it is easy to make it into a globular form especially, a ferrite with good mobility or magnetite is used suitably. Especially the shape of a core agent cannot interfere a globular form, an infinite form, etc., and can use them. Although mean particle diameter is generally 10-500 micrometers, in order to print high resolution images, 30-80 micrometers is preferred.

[0075]As coating resin which covers these core agents, For example, polyethylene, polypropylene, polystyrene, polyacrylonitrile, Polyvinyl acetate, polyvinyl alcohol, a polyvinyl butyral, Polyvinyl chloride, a polyvinyl carbazole, polyvinyl ether, polyvinyl ketone, VCM/PVC/vinyl acetate copolymer, styrene/acrylic copolymer, straight silicone resin that consists of an ORGANO siloxane bond, or its denaturation article, A fluoro-resin, an acrylic resin (meta), polyester, polyurethane, polycarbonate, phenol resin, amino resin, melamine resin, benzoguanamine resin, a urea resin, amide resin, an epoxy resin, acrylic polyol resin, etc. can be used. Also in these, especially silicone resin, a fluoro-resin, and an acrylic resin (meta) are excellent in electrifying stability, covering intensity, etc., and can use it more conveniently. That is, as for a resin coated carrier used by this invention, it is preferred that it is the resin coating magnetic carrier covered with one or more sorts of resin chosen from silicone resin, a fluoro-resin, and an acrylic resin (meta) using a ferrite or magnetite as a core agent.

[0076]When using color toner for electrostatic charge image development of this invention as a toner for one ingredient of nonmagnetic development, it is preferred to use as a toner for one ingredient of nonmagnetic development of a contact type. One ingredient of nonmagnetic developing method of a contact type is a method of developing an electrostatic latent image which carried out frictional electrification and was formed subsequently to the surface of a photo conductor, when a toner passes through between a developing sleeve and layer thickness regulating members welded by pressure to it.

[0077]In this case, especially if it is anticipated-use conditions, construction material of an electrification grant member of a developer, etc. will not be limited. For example, a developing sleeve made of aluminum, stainless steel, urethane rubber, and silicone rubber, aluminum, stainless steel, duralumin, copper, or a layer thickness regulating member that pasted urethane rubber and silicone rubber together to them can use it conveniently.

[0078]Composition of a developer which was suitable in order that color toner for electrostatic

charge image development of this invention might reveal an effect when it used as a toner for one ingredient of nonmagnetic development, Either of a developing sleeve and a layer thickness regulating member is a case where it is metal, such as aluminum and stainless steel, and the most effective combination (a developing sleeve/layer thickness regulating member), It is the combination of a layer thickness regulating member of combination of a developing sleeve made of urethane rubber or silicone rubber, and a layer thickness regulating member made from stainless steel, a developing sleeve made from stainless steel and urethane rubber, or a product made of silicone rubber.

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[Translation done.]

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

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EXAMPLE

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[Example]Hereafter, this invention is explained still in detail using working example and a comparative example. The numerical value in a presentation table expresses a "weight section" below. The synthetic example of the binder resin which was used in preparing a toner first is shown below.

(Synthetic example 1)

Naphthalene-dicarboxylic-acid 87 weight-section terephthalic acid 249 weight-section diethylene-glycol 26 weight-section neopentyl glycol 104 weight-section ethylene glycol 50 weight-section tetrabutyl titanate the raw material of 2.5 or more weight sections. It put into the 4 Thu mouth flask glass [ 2L ], and the thermometer, the stirring rod, and the nitrogen introducing pipe were attached, it decompressed one by one after a 10-hour reaction at 240 \*\* under the ordinary pressure nitrogen air current in the electric heat mantle heater, and the reaction was continued by 10mmHg. The reaction was pursued by the softening temperature according to ASTM-E 28-517, and when softening temperature amounted to 101 \*\*, it ended the reaction. The obtained polymer (it expresses the resin A hereafter) is a colorless solid. The acid value 7, the glass transition temperature of 70 \*\* by a DSC measurement method, and softening temperature were 102 \*\*.

[0080](Synthetic example 2)

Terephthalic acid 315 weight-section diethylene-glycol 21 weight-section cyclohexane dimethanol 144 weight-section ethylene glycol 50 weight-section tetrabutyl titanate It reacted like the example 1 of resin composition using the raw material of 2.5 or more weight sections. The obtained polymer (it expresses the resin B hereafter) is a colorless solid. The acid value 9, the glass transition temperature of 60 \*\* by a DSC measurement method, and softening temperature were 97 \*\*.

[0081]

(Synthetic example 3)

Polyoxyethylene (2.0)-2,2-bis(4-hydronalium KISHIFE nil)propane 64 weight section Isophthalic acid 16 weight section Terephthalic acid 16 weight section Maleic anhydride 0.6 weight section Dibutyltin oxide the raw material of 0.06 or more weight sections. It put into the 4 Thu mouth flask glass [ 2L ], and the thermometer, the stirring rod, and the nitrogen introducing pipe were attached, it decompressed one by one after a 24-hour reaction at 230 \*\* under the ordinary pressure nitrogen air current in the electric heat mantle heater, and the reaction was continued by 10mmHg. The reaction was pursued by the softening temperature according to ASTM-E 28-517, and when softening temperature amounted to 99 \*\*, it ended the reaction.

[0082]The obtained polymer (it expresses the resin C hereafter) is a colorless solid.

The acid value 7, the glass transition temperature of 62 \*\* by a DSC measurement method, and softening temperature were 101 \*\*.

[0083]

(Synthetic example 4)

Terephthalic acid 332 weight section Isophthalic acid . 332 weight sections Polyoxypropylene (2.2)-2,2-bis(4-hydronalium KISHIFE nil)propane 700 weight section Trimethylolpropane 80 weight section Ethylene glycol 75 weight section The tetrabutyl titanate 3 weight-section above-mentioned compound Stirrer, It puts into the 4 mouth flask which set the capacitor and the thermometer, and it was made to react by ordinary pressure at 240 \*\* under a nitrogen gas air current for 10 hours, removing the water generated by dehydration condensation. It decompressed one by one after that, and the reaction was continued by 10mmHg. The reaction was pursued by softening temperature, and when softening temperature amounted to 151 \*\*, it ended the reaction. Tg according [ according to / in the softening temperature of the obtained polymer (it expresses the resin D hereafter) / 153 \*\* / acid value ] to 4 and a DSC measurement method was 65 \*\*.

[0084](Synthetic example 5)

Isophthalic acid 116 weight-section terephthalic acid 166 weight-section trimellitic anhydride 38 weight-section diethylene-glycol 26 weight-section neopentyl glycol 104 weight-section ethylene glycol 50 weight-section tetrabutyl titanate the raw material of 2.5 or more weight sections. It put into the 4 Thu mouth flask glass [ 2L ], and the thermometer, the stirring rod, and the nitrogen introducing pipe were attached, it decompressed one by one after a 10-hour reaction at 240 \*\* under the ordinary pressure nitrogen air current in the electric heat mantle heater, and the reaction was continued by 10mmHg. The reaction was pursued by the softening temperature according to ASTM-E 28-517, and when softening temperature amounted to 148 \*\*, it ended the reaction. The obtained polymer (it expresses the resin E hereafter) is a colorless solid.

The acid value 4, the glass transition temperature of 72 \*\* by a DSC measurement method, and softening temperature were 151 \*\*.

[0085]T1/2 temperature measured using Shimadzu flow tester CFT-500 which is a constant stress extrusion type small tube type rheometer defines the softening temperature of resin. The measuring condition in the flow tester was performed on with piston cross-section area 1cm<sup>2</sup>, cylinder pressure 0.98MPa, die 1 mm in length, the diameter of a die hole of 1 mm, measurement start temperature 50degreeC, heating-rate C/min of 6 degrees, and a sample weight of 1.5 g conditions.

[0086]

<The example of manufacture of a processing pigment> (processing pigment 1)

Organic color of resin A 650 weight section <formula 2> The raw material of 350 or more weight sections was kneaded with the two heating roll after mixing with the Henschel mixer. After-cooling coarse grinding was performed and the processing pigment 1 of 35% of pigment content was produced.

[0087](Processing pigment 2) The processing pigment 2 was produced completely like the case where the processing pigment 1 is produced, except using the resin A in production of the processing pigment 1 as the resin B.

[0088](Processing pigment 3) The processing pigment 3 was produced completely like the case where the processing pigment 1 is produced, except using the organic color of the formula 2 in production of the processing pigment 1 as the organic color of the formula 8.

[0089](Processing pigment 4) The processing pigment 4 was produced completely like the case where the processing pigment 1 is produced, except using the resin A in production of the processing pigment 1 as the resin E.

[0090](Processing pigment 1 for comparison) The processing pigment 1 for comparison was produced completely like the case where the processing pigment 1 is produced, except using the resin A in production of the processing pigment 1 as the resin C.

[0091](Processing pigment 2 for comparison) The processing pigment 2 for comparison was produced completely like the case where the processing pigment 1 is produced, except using the resin A in production of the processing pigment 1 as the resin D.

[0092](Processing pigment 3 for comparison) In the above-mentioned processing pigment 1, the

processing pigment 3 for comparison was similarly obtained instead of the organic color of the formula 2 except having used the C.I. pigment red 122.

[0093](Processing pigment 4 for comparison) In the above-mentioned processing pigment 1, the processing pigment 4 for comparison was similarly obtained instead of the organic color of the formula 2 except having used the C.I. pigment red 57:1.

[0094](Processing pigment 5 for comparison) In the above-mentioned processing pigment 4, the processing pigment 5 for comparison was similarly obtained instead of the organic color of the formula 2 except having used the C.I. pigment red 122.

[0095](Processing pigment 6 for comparison) In the above-mentioned processing pigment 4, the processing pigment 6 for comparison was similarly obtained instead of the organic color of the formula 2 except having used the C.I. pigment red 57:1.

[0096](Working example 1) Resin A93 weight section, paints (Carmine 190 (made by Arimoto chemicals company)) 4 weight section of the formula 2, Charge controlling agent (compound [ of the above <charge controlling agent 4> ], LR-147 (made by Japan Carlit Co., Ltd.)) 1 weight section, The amount part of carnauba wax (refining carnauba wax No.1, acid value 5, product made from SERARIKA NODA) duplex was mixed with the Henschel mixer, melt kneading was carried out with the biaxial kneading machine, it pulverized and classified with the after-cooling jet mill, and the toner with a mean particle diameter of 8.0 micrometers was produced. [0097] Next, the magenta toner of working example 1 was obtained to this toner 100 weight section by carrying out externally adding of silica "NAX50" made from Japanese Aerosil 1 weight section, and the "RY-200" 1 weight section.

[0098]By similarly, carrying out melt kneading, grinding and classifying resin, an organic color (or processing pigment), a charge controlling agent, and WAX after cooling, with a biaxial kneading machine, by the presentation shown in Table 1, after fully mixing with a Henschel mixer, The toner of working example 2-8 and the comparative examples 1-5 was obtained by manufacturing a toner and also performing an externally adding process like working example 1.

[0099]

[Table 1]

表 1

	樹脂	着色剤	WAX	帯電制御剤	体積平均 ( $\mu m$ )
実施例 1	樹脂 A 9 3 部	式 2 の顔料 4 部	加ナハ WAX 2 部	帯電制御剤 4 1 部	8.0
実施例 2	樹脂 A 8 5 部	加工顔料 1 1 2 部	加ナハ WAX 2 部	帯電制御剤 4 1 部	7.8
実施例 3	樹脂 B 8 5 部	加工顔料 2 1 2 部	加ナハ WAX 2 部	帯電制御剤 1 1 部	7.8
実施例 4	樹脂 A 8 5 部	加工顔料 3 1 2 部	加ナハ WAX 2 部	帯電制御剤 4 1 部	7.8
実施例 5	樹脂 A 8 5 部	加工顔料 1 1 2 部	P P WAX 2 部	帯電制御剤 4 1 部	8.1
実施例 6	樹脂 A 8 5 部	加工顔料 1 1 2 部	加ナハ WAX 2 部	E-8 4 1 部	8.0
実施例 7	樹脂 B 8 5 部	加工顔料 2 1 2 部	P E T B 2 部	帯電制御剤 4 1 部	7.8
実施例 8	樹脂 A 8 5 部	加工顔料 3 1 2 部	P E T B 2 部	帯電制御剤 4 1 部	8.0
比較例 1	樹脂 A 9 2 部	P. R. 122 5 部	加ナハ WAX 2 部	帯電制御剤 4 1 部	7.8
比較例 2	樹脂 A 9 3 部	P. R. 57:1 4 部	加ナハ WAX 2 部	帯電制御剤 4 1 部	7.9
比較例 3	樹脂 C 8 5 部	比較用加工顔料 1 1 2 部	加ナハ WAX 2 部	帯電制御剤 4 1 部	7.9
比較例 4	樹脂 A 8 5 部	比較用加工顔料 3 1 2 部	加ナハ WAX 2 部	帯電制御剤 4 1 部	7.9
比較例 5	樹脂 A 8 5 部	比較用加工顔料 4 1 2 部	加ナハ WAX 2 部	帯電制御剤 4 1 部	8.0

[0100]The passage of the following [ cable address / in Table 1 ]. A part expresses a weight section.

- P.R.122:C.I. pigment red 122 (Fastogen Super Magenta R "Dainippon Ink & Chemicals, Inc. make")

- P.R.57:1;C.I. pigment red 57:1 (Symuler Brilliant Carmin six B285 "Dainippon Ink & Chemicals, Inc. make")
- PETB; -- tetrabehenic acid ester carnauba wax [ of pentaerythritol ]; -- refining carnauba wax No.1 (the acid value 5, product made from SERARIKA NODA)
- PPWAX; screw call 660P (polypropylene wax "Mitsuhiro transformation make")
- E-84; BONTORON E-84 (metal complex compound of salicylic acid "Orient chemicals company make")

[0101](Evaluation of the toner of Table 1) An exclusive toner is extracted from the cartridge of the printer (the "IPUSHIO color 2000" by Ricoh Co., Ltd.) of commercial one ingredient of nonmagnetic development system, The washed cartridge was filled up with the toner of working example and the comparative example which were shown in Table 1, and continuous printing of 10000 sheets was performed with 5% of image concentration. In order to evaluate the stability of the printing image to change of an environmental condition, the continuous printing examination was carried out under 25 \*\*, 50%, 32 \*\*, and 85% of two environment.

[0102](1) The image concentration and the greasing of image concentration, a greasing, and electrification quantity printed matter were measured by Macbeth densimeter RD-918. The greasing deducted and asked for the blank paper concentration before a print from the white part concentration after printing. \*\* and the time or more of 0.03 were made [ the time of the difference being less than 0.01 ] into x for O and the time of 0.01 to less than 0.03. The electrification quantity of the printing toner was measured using suction type small electrification quantity measuring device Mode210HS (made in Thorek).

[0103]A toner falls from the developing sleeve with which the cartridge was equipped after 10000 toner omission and toner scattering printing, or (2) (Toner omission), The state where \*\*, a lot of toner omissions, or toner scattering was accepted in the state where O, a little toner omissions, or toner scattering is accepted in the state where scatter around a developer and the inside of a machine (toner scattering) is not soiled was judged to be x.

[0104](3) Using the OHP transparency above-mentioned printer, the undecidedness arrival picture was formed on the OHP sheet, and the undecidedness arrival picture was established at 140 \*\* with the fixing unit used by the above-mentioned fixing / offset examination.

[0105]The OHP sheet created by the above procedure was projected on the white screen with the over head projector, and color definition was evaluated. Evaluation was performed visually, it was clear, and when it was the blackish projection image which has \*\* and muddiness in O and the case where transparency is a little missing and there is some muddiness if it is a transparent good projection picture, it was considered as x.

[0106]A result [ in / for the result in 25 \*\* and 50% / to Table 2 / 32 \*\* and 85% ] is shown in Table 3.

[0107]

[Table 2]

表 2

	ト 落ちト 飛散 初期 / 10000枚	画像濃度 初期 / 10000枚	地汚れ 初期 / 10000枚	帯電量 ( $\mu C/g$ )	OHP 透明性
実施例 1	O / $\Delta$	1.39 / 1.42	O / O	-10.5	$\Delta$
実施例 2	O / O	1.37 / 1.39	O / O	-12.0	O
実施例 3	O / O	1.39 / 1.42	O / O	-12.8	O
実施例 4	O / O	1.38 / 1.41	O / O	-12.7	O
実施例 5	O / O	1.36 / 1.39	O / O	-13.8	O
実施例 6	O / $\Delta$	1.40 / 1.46	O / O	-10.0	O
実施例 7	O / O	1.36 / 1.37	O / O	-12.5	O
実施例 8	O / O	1.39 / 1.41	O / O	-12.5	O
比較例 1	$\Delta$ / x	1.33 / 1.59	O / $\Delta$	-8.5	x
比較例 2	O / x	1.38 / 1.48	$\Delta$ / x	-9.2	$\Delta$
比較例 3	O / O	1.38 / 1.41	O / O	-12.3	O
比較例 4	O / $\Delta$	1.33 / 1.45	O / $\Delta$	-9.8	O
比較例 5	O / $\Delta$	1.33 / 1.45	O / $\Delta$	-9.7	O

[0108]

[Table 3]



表3

	トナー落ちトナー飛散 初期/10000枚	画像濃度 初期/10000枚	地汚れ 初期/10000枚	帯電量 ( $\mu\text{C/g}$ )	OHP 透明性
実施例1	○/△	1.36/1.30	○/○	-9.5	△
実施例2	○/○	1.34/1.30	○/○	-11.1	○
実施例3	○/○	1.36/1.31	○/○	-12.3	○
実施例4	○/○	1.35/1.31	○/○	-12.0	○
実施例5	○/○	1.33/1.28	○/○	-12.5	○
実施例6	○/△	1.38/1.44	○/○	-8.9	○
実施例7	○/○	1.33/1.30	○/○	-11.6	○
実施例8	○/○	1.37/1.33	○/○	-12.2	○
比較例1	△/×	1.28/1.22	○/×	-7.7	×
比較例2	○/×	1.32/1.10	△/×	-5.1	△
比較例3	○/△	1.35/1.25	○/△	-12.2	○
比較例4	○/×	1.28/1.16	○/×	-6.1	○
比較例5	○/×	1.27/1.16	○/×	-6.1	○

[0109](4) The non-fixed image sample of A-4 paper size is produced with the test machine which converted the printer of one ingredient of nonmagnetic development system of fixing/offset test marketing by heat roll fixing. Fixing starting temperature and the existence of the offset phenomenon were checked in the following test condition using the heat roll fixing unit of the following specification.

ロール材質           上：四弗化エチレン  
                           下：HTVシリコーン  
 ロール形状           径：50mm  
                           長さ：370mm  
 上ロール荷重        ： 7kg  
 上/下ロールニップ幅   ： 4mm  
 紙送り速度           ： 100mm/sec

In order to measure fixing starting temperature, it asked for the image concentration residual ratio calculated by the following formula.

[0110]Image concentration residual ratio = after [ a fastness test ] image concentration / said left examination previous image concentration \* image concentration was measured in Macbeth image concentration meter RD-918.

\* The image concentration after a fastness test is the image concentration after grinding a fixed image using a Gakushin-type fastness-to-rubbing testing machine (load: 200 g, grinding operation:5 stroke).

It was considered as the level which is satisfactory practically by not less than 80% of the image concentration residual ratio, and the minimum temperature was made into fixing starting temperature.

[0111]Offset starting temperature observed the fixed image sample, and made it the temperature an offset phenomenon is visually accepted to be. The result was shown in Table 4.

[0112]

[Table 4]

表4

	定着開始温度／オフセット開始温度 °C
実施例1	130-210
実施例2	130-210
実施例3	125-210
実施例4	130-210
実施例5	140-210
実施例6	130-210
実施例7	125-210
実施例8	130-210
比較例1	130-210
比較例2	130-210
比較例3	140-210
比較例4	130-210
比較例5	130-210

[0113](Working example 9) Resin E85 weight section and the processing pigment 4 as 12 weight sections and a charge controlling agent TP-415(product made from Hodogaya chemicals)1 weight section of quarternary-ammonium-salt structure, The amount part of carnauba wax (refining carnauba wax No.1, acid value 5, product made from SERARIKA NODA) duplexs was mixed with the Henschel mixer, melt kneading was carried out with the biaxial kneading machine, it pulverized and classified with the after-cooling jet mill, and the toner with a mean particle diameter of 8.0 micrometers was produced.

[0114]Next, the positive triboelectric charging magenta toner of working example 9 was obtained to this toner 100 weight section by carrying out externally adding of the silica "TG820F" made from Cabot Specialty Chemicals ink1 weight section. Subsequently, this toner 5 weight section and ferrite carrier 95 weight section with a mean particle diameter of 80 micrometers which covered silicone resin were mixed with the ball mill, and it was considered as the two component developer.

[0115]By similarly, carrying out melt kneading, grinding and classifying resin, an organic color (or processing pigment), a charge controlling agent, and WAX after cooling, with a biaxial kneading machine, by the presentation shown in Table 5, after fully mixing with a Henschel mixer, The toner of the comparative examples 6-8 was obtained by manufacturing a toner and also performing an externally adding process like working example 9.

[0116]

[Table 5]

表5

	樹脂	着色剤	WAX	帯電制御剤	体積平均径 ( $\mu\text{m}$ )
実施例 9	樹脂E 8.5部	加工顔料4 1.2部	カルバ WAX 2部	TP-415 1部	8.0
比較例 6	樹脂D 8.5部	比較用加工顔料2 1.2部	カルバ WAX 2部	TP-415 1部	7.8
比較例 7	樹脂E 8.5部	比較用加工顔料5 1.2部	カルバ WAX 2部	TP-415 1部	7.9
比較例 8	樹脂E 8.5部	比較用加工顔料6 1.2部	カルバ WAX 2部	TP-415 1部	7.9

[0117](Evaluation of the toner of Table 5)

[0118](1) Using a commercial laser beam printer (selenium photo conductor loading) by the two component developer of the printing torture test table 5 under 25 \*\*, 50% and 32 \*\*, and 85% of conditions, Performed printing of 50000 sheets, and the concentration and greasing concentration of the picture part before and behind a continuous print were measured, and the electrification quantity of the developer was measured. Image concentration and a greasing were measured by Macbeth densimeter RD-918. The greasing deducted and asked for the blank paper concentration before a print from the white part concentration after printing. \*\* and the time or more of 0.03 were made [ the time of the difference being less than 0.01 ] into x for O and the time of 0.01 to less than 0.03.

[0119] Visual observation of the scattering situation of the toner inside the development counter after 50000-sheet printing was carried out. Although O and scattering could hardly be seen in the state where scattering is not observed at all, when the inside of a device was wiped with the waste cloth, the state where x and severe scattering inside the plane could check the state where \*\* and scattering inside the plane can check visually the state where toner soiling is observed was made into xx.

[0120] About electrification quantity, the toner was extracted from the inside of a developer and it measured with blowing off electrification quantity measuring apparatus (made by Toshiba Chemical).

[0121] A result [ in / for the result in 25 \*\* and 50% / to Table 6 / 32 \*\* and 85% ] is shown in Table 7.

[0122]

[Table 6]

表 6

	画像濃度 初期／50000枚	地汚れ 初期／50000枚	帯電量 ( $\mu\text{C/g}$ )	トナーの飛散状況
実施例 9	1.33／1.36	○／○	18.5	○
比較例 6	1.32／1.38	○／○	16.8	○
比較例 7	1.36／1.47	○／△	20.5	×
比較例 8	1.35／1.46	○／△	16.5	×

[0123]

[Table 7]

表 7

	画像濃度 初期／50000枚	地汚れ 初期／50000枚	帯電量 ( $\mu\text{C/g}$ )	トナーの飛散状況
実施例 9	1.38／1.40	○／○	17.8	○
比較例 6	1.35／1.43	○／△	14.8	△
比較例 7	1.38／1.49	○／×	19.6	×
比較例 8	1.37／1.47	○／×	15.8	×

[0124](2) The non-fixed image sample was produced using the method of fixing/offset test above by heat roll fixing, and fixing starting temperature and offset starting temperature were investigated using the same heat roll fixing unit as the first half. A test result is shown in Table 8.

[0125]

[Table 8]

表 8

	定着開始温度／オフセット開始温度 ℃
実施例	140-220
比較例	150-220
比較例	140-220
比較例	140-220

[0126]

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[Translation done.]

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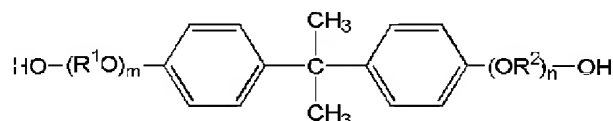
(51) Int.Cl. <sup>7</sup>	識別記号	F I	テーマト* (参考)
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(71) 出願人	000002886 大日本インキ化学工業株式会社 東京都板橋区坂下3丁目35番58号		
(72) 発明者	小倉 克之 埼玉県さいたま市大和田町1-1662-9		
(72) 発明者	中村 正延 埼玉県蕨市中央1-17-30ルネ蕨1-709		
(74) 代理人	100088764 弁理士 高橋 勝利		
Fターム(参考)	2H005 AA01 AA05 AA21 AB04 CA08 CA14 CA21 DA01		

(54) 【発明の名称】 静電荷像現像用カラートナー及びその製造方法

(57) 【要約】

【課題】 優れた着色力及び色相を有し、温度、湿度等の環境が変動しても、安定した帯電特性を示し、色再現性に優れ、良好かつ安定な印字画質を示し、また、良好な定着性を示し、耐オフセット性にも優れた赤色カラートナー、特にマゼンタトナーを提供する。

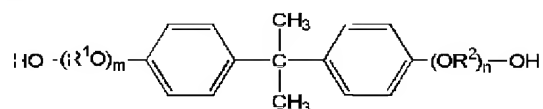
【解決手段】 バインダー樹脂および着色剤を含有する静電荷像現像用カラートナーにおいて、前記バインダー樹脂が、(A) 2価以上の多塩基酸、酸無水物及びこれらの低級アルキルエステルからなる群より選ばれる1種以上の多塩基酸化合物と (B) 2価以上の脂肪族アルコールを主成分として反応させて得られるポリエステル樹脂を含有し、前記着色剤が、C. I. Pigment Red 150、31、147、176、187、188、269の中から選択される1種又はそれ以上の有機顔料であることを特徴とする静電荷像現像用カラートナーを用いる。



【特許請求の範囲】

【請求項1】 バインダー樹脂および着色剤を含有する静電荷像現像用カートナーにおいて、前記バインダー樹脂が、(A) 2価以上の多塩基酸、酸無水物及びこれらの低級アルキルエステルからなる群より選ばれる1種以上の多塩基酸化合物と (B) 2価以上の脂肪族アルコールを主成分〔但し、式1、

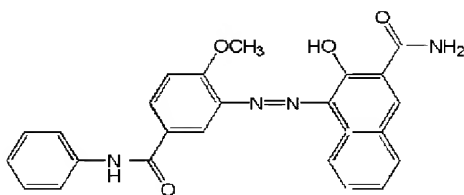
【化1】



(式1)

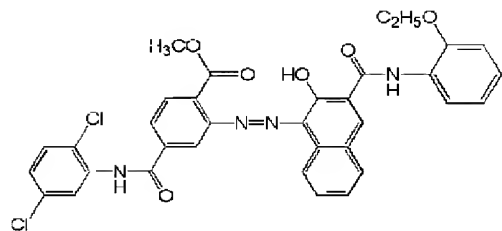
(式中、R<sup>1</sup> 及びR<sup>2</sup> は、同一又は異なってエチレン基又はプロピレン基を示し、m、nは、同一又は異なって0～7の整数を示し、かつm+nは0～7の整数を示す。)で表されるビスフェノール骨格を有する化合物を除く〕として反応させて得られるポリエステル樹脂を含有し、前記着色剤が式2、式3、式4、式5、式6、式7、式8、

【化2】



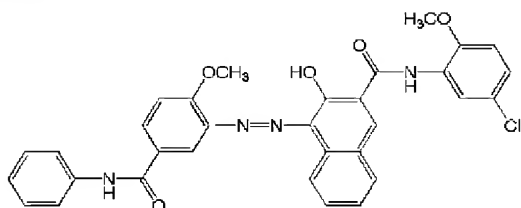
(式6)

【化7】



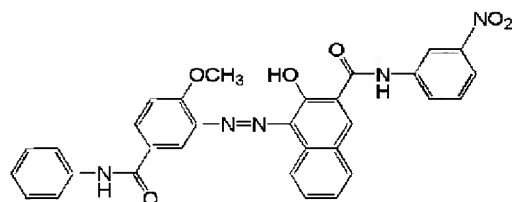
(式7)

【化8】



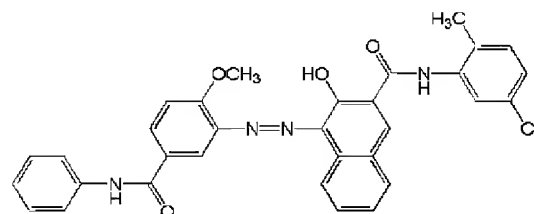
(式2)

【化3】



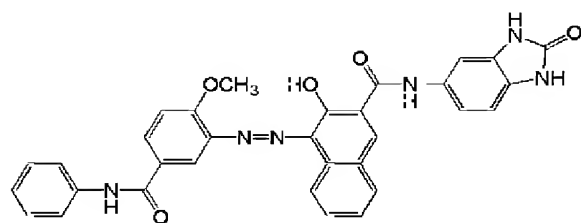
(式3)

【化4】



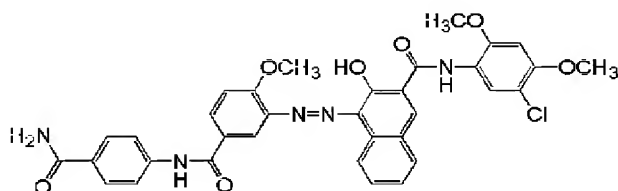
(式4)

【化5】



(式5)

【化6】



(式8)

の中から選択される1種又はそれ以上の有機顔料であることを特徴とする静電荷像現像用カートナー。

【請求項2】 更に離型剤を含有する請求項1記載の静電荷像現像用カートナー。

【請求項3】 前記離型剤が高級脂肪酸エステル化合物及び／又は脂肪族アルコール化合物を含有するワックスである請求項2記載の静電荷像現像用カートナー。

【請求項4】 更に帯電制御剤を含有する請求項1記載の静電荷像現像用カートナー。

【請求項5】 前記式2、式3、式4、式5、式6、式7、式8の中から選択される1種又はそれ以上の有機顔料を前記バインダー樹脂の一部を用いて、予め分散処理を行った後、さらに前記バインダー樹脂を用いて希釈分散するカートナーの製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、電子写真、静電記録、静電印刷などにおける静電荷像を現像するための静電荷像現像用カラートナー及びその製造方法に関する。

【0002】

【従来の技術】電子写真法により可視画像を得るためのトナー組成物として、多くはカーボンブラックの如き黒色着色剤をバインダー樹脂中に分散させたものが多く使用されている。しかしながら、最近では、シアン顔料、マゼンタ顔料、イエロー顔料、又はその他の有彩色顔料をバインダー中に分散させたカラートナーも使用されており、これらのカラートナーを用いたフルカラーあるいはモノカラーの複写機、プリンターが開発されている。

【0003】このようなカラートナーに要求される特性としては、印刷後の画像が鮮やかな発色性を有すること、多色印刷を行った際の色重ねにおいて優れた透明性を発揮して色濁りの生じない鮮明な色再現性を有すること、あるいは、オーバーヘッドプロジェクター（以下、OHPという）シート上に転写・定着して得たカラー画像をスクリーン上に投影した際に濁りのない鮮明な色を写し出すこと、等の色再現特性が求められている。

【0004】従来より、このようなカラートナーに関して多くの技術が開示されており、特にマゼンタ色あるいは赤色のカラートナーに関しては、有機顔料としてキナクリドン系の顔料であるC. I. PIGMENT RED 122、あるいはレーキ顔料であるC. I. PIGMENT RED 57:1が主として用いられてきた。前者は、色相が良好であり、ブルー系の色再現性に優れているが、トナー用の樹脂に対する分散性が悪く、着色力が劣る。したがって、目的とする濃度の印刷を行うためにはトナー中の含有量を多くしなければならず、その結果、トナーの帯電特性が不安定になり易いという欠点を有している。特に、顔料としては正帯電性となり易く、負帯電性トナーに適用した場合、使用中に帯電量が、低下するといった問題があった。

【0005】また、後者においては、着色力は良好であるが、Ca塩構造を採っているため、吸湿性があり、トナーの帯電特性が環境の影響を受けやすいという欠点がある。また、C. I. PIGMENT RED 57:1は印刷インキに使用した場合は鮮明なマゼンタ色が得られるが、トナーに使用した場合は、黄味のマゼンタ色となる傾向があり、色相としては、C. I. PIGMENT RED 122に比べて劣っていた。

【0006】このような背景から、トナー分野においては、優れた着色力及び色相を有し、温度、湿度等の環境が変動しても、安定した帯電特性を示し、その結果として、色再現性に優れ、さらに負帯電性トナーに適用した場合も使用中に帯電量が変動せず、良好かつ安定な印字画質を示す赤色カラートナー、特にマゼンタトナーを得ることが望まれてきた。

【0007】さらに、トナー画像を定着する方式として

は、ヒートロール定着方式が広く一般的に用いられているが、その際における良好な定着性及び耐オフセット性もカラートナーに求められる重要な特性である。最近のカラー複写機、あるいはプリンターにおいては、処理速度の高速化が行われており、定着温度はより低温に、定着時間もより短時間となってきた。したがって、最近のカラートナーにおいては、より低温且つ低エネルギーで定着し、また広い温度範囲で耐オフセット性を有することが、前記の色再現性、帯電特性の改善と共に求められている。

【0008】

【発明が解決しようとする課題】本発明の目的は、優れた着色力及び色相を有し、温度、湿度等の環境が変動しても、安定した帯電特性を示し、その結果として、色再現性に優れ、さらに負帯電性トナーに適用した場合も使用中に帯電量が変動せず、良好かつ安定な印字画質を示す赤色カラートナー、特にマゼンタトナーを提供することにある。

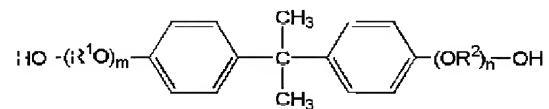
【0009】また、本発明の他の目的は低温定着、あるいは短時間定着のような低エネルギー定着条件においても良好な定着性を示し、耐オフセット性にも優れた赤色カラートナー、特にマゼンタトナーを提供することにある。

【0010】また、本発明の他の目的は、上記特性を満足する赤色カラートナー、特にマゼンタトナーの製造方法を提供することにある。

【0011】

【課題を解決するための手段】本発明者らは、上記の課題を解決すべく鋭意研究を重ねた結果、本発明を完成するに至った。即ち、本発明は、バインダー樹脂および着色剤を含有する静電荷像現像用カラートナーにおいて、前記バインダー樹脂が、(A) 2価以上の多塩基酸、酸無水物及びこれらの低級アルキルエステルからなる群より選ばれる1種以上の多塩基酸化合物と(B) 2価以上の脂肪族アルコールを主成分〔但し、式1、

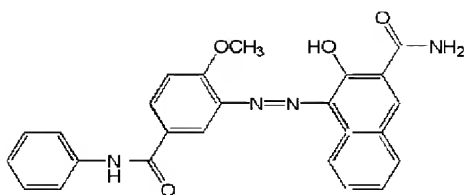
【化9】



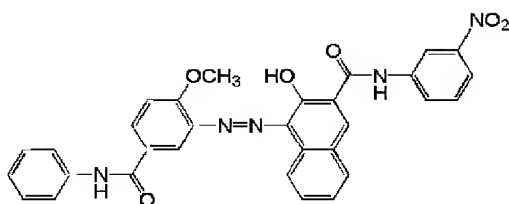
(式1)

(式中、R<sup>1</sup>及びR<sup>2</sup>は、同一又は異なってエチレン基又はプロピレン基を示し、m、nは、同一又は異なって0～7の整数を示し、かつm+nは0～7の整数を示す。)で表されるビスフェノール骨格を有する化合物を除く〕として反応させて得られるポリエステル樹脂を含有し、前記着色剤が式2、式3、式4、式5、式6、式7、式8、

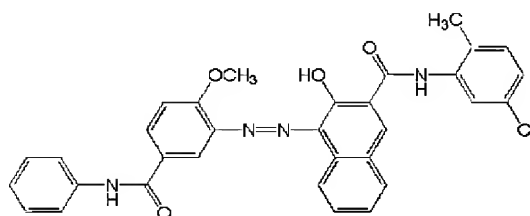
【化10】



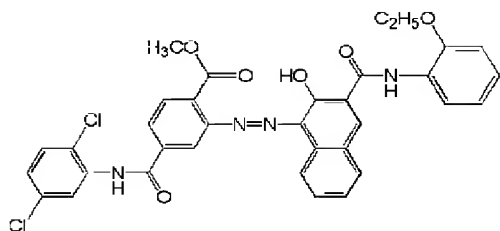
(式2)  
【化11】



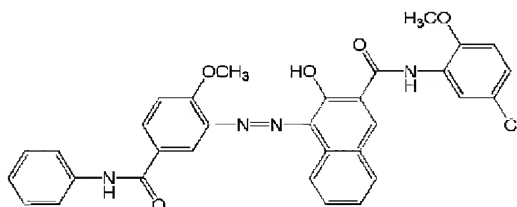
(式3)  
【化12】



(式6)  
【化15】



(式7)  
【化16】

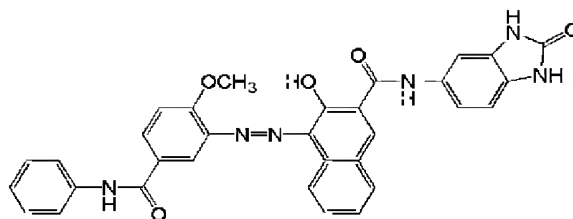


(式8)

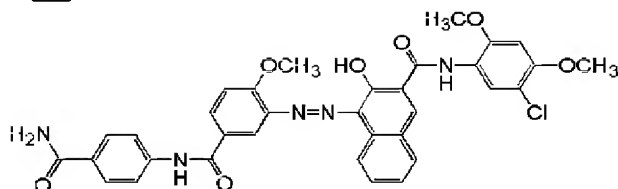
の中から選択される1種又はそれ以上の有機顔料であることを特徴とする静電荷像現像用カラートナーを提供するものである。

【0012】また、本発明は、前記式2、式3、式4、

(式4)  
【化13】



(式5)  
【化14】



式5、式6、式7、式8の中から選択される1種又はそれ以上の有機顔料を前記バインダー樹脂の一部を用いて、予め分散処理を行った後、さらに前記バインダー樹脂を用いて希釈分散するカラートナーの製造方法を提供するものである。

【0013】

【発明の実施の形態】以下、本発明を詳しく説明する。本発明の静電荷像現像用カラートナーに用いるバインダー樹脂はポリエステル樹脂である。

【0014】本発明で用いられるポリエステル樹脂を製造するための、2価以上の多塩基酸及び／又は酸無水物及び／又はこれらの低級アルキルエステルから選ばれる多塩基酸化合物(A)としては、例えば無水フタル酸、テレフタル酸、イソフタル酸、オルソフタル酸、ナフタレンジカルボン酸、アジピン酸、マレイン酸、無水マレイン酸、フマル酸、イタコン酸、シトラコン酸、ヘキサヒドロ無水フタル酸、テトラヒドロ無水フタル酸、シクロヘキサジカルボン酸、コハク酸、マロン酸、グルタル酸、アゼライン酸、セバシン酸等のジカルボン酸又はその誘導体又はそのエステル化物が、また、例えばトリメリット酸、無水トリメリット酸、ピロメリット酸、無水ピロメリット酸等の三官能以上の多価カルボン酸又は

その誘導体又はそのエステル化物が挙げられる。

【0015】また、2価以上の脂肪族アルコール(B)としては、例えば1,4-シクロヘキサジメタノール、エチレングリコール、ジエチレングリコール、トリエチレングリコール、プロピレングリコール、ジプロピレングリコール、トリプロピレングリコール、ブタンジオール、ペンタンジオール、ヘキサジオール、ポリエチレングリコール、ポリプロピレングリコール、エチレンオキサイド-プロピレンオキサイドランダム共重合体ジオール、エチレンオキサイド-プロピレンオキサイドブロック共重合体ジオール、エチレンオキサイド-テトラヒドロフラン共重合体ジオール、ポリカプロラクトンジオール等のジオールが、また、ソルビトール、1,2,3,6-ヘキサントリオール、1,4-ソルビタン、ペンタエリスリトール、1,2,4-ブタントリオール、1,2,5-ペンタントリオール、グリセリン、2-メチルプロパントリオール、2-メチル-1,2,4-ブタントリオール、トリメチロールエタン、トリメチロールプロパン、1,3,5-トリメチロールベンゼン、等の三官能以上の多価アルコールが挙げられる。

【0016】また、1分子中に2個以上のグリシジル基を有する化合物も上記(A)のカルボン酸化合物と反応する2価以上の脂肪族アルコール(B)として用いることもできる。具体的には、例えば、ネオペンチルグリコールジグリシジルエーテル、グリセリントリグリシジルエーテル、トリメチロールプロパントリグリシジルエーテル、トリメチロールエタントリグリシジルエーテル、ペンタエリスリトールテトラグリシジルエーテル、等がある。

【0017】また、本発明では性能に影響を与えない範囲において芳香族ジオールあるいは3価以上の多価アルコールを併用することもできる。芳香族ジオールあるいは3価以上の多価アルコールとしては、例えばカテコール、レゾルシノール、ヒドロキノン、ビスフェノールA型エポキシ樹脂、ビスフェノールF型エポキシ樹脂、ビスフェノールS型エポキシ樹脂、クレゾールノボラック型エポキシ樹脂、フェノールノボラック型エポキシ樹脂、等が挙げられる。ただし、上記式1で表されるビスフェノールA骨格を有する化合物は除く。除かれる芳香族ジオールとしては、例えばビスフェノールA、ポリオキシエチレン-(2,2)-2,2-ビス(4-ヒドロキシフェニル)プロパン、ポリオキシエチレン-(2,0)-2,2-ビス(4-ヒドロキシフェニル)プロパン、ポリオキシプロピレン-(2,0)-2,2-ビス(4-ヒドロキシフェニル)プロパン、ポリオキシプロピレン-(2,2)-ポリオキシエチレン-(2,0)-2,2-ビス(4-ヒドロキシフェニル)プロパン、ポリオキシプロピレン-(6)-2,2-ビス(4-ヒドロキシフェニル)プロパン、ポリオキシプロピレン-(2,2)-2,2-ビス(4-ヒドロキシフェニル)

プロパン、ポリオキシプロピレン-(2,4)-2,2-ビス(4-ヒドロキシフェニル)プロパン、ポリオキシプロピレン-(3,3)-2,2-ビス(4-ヒドロキシフェニル)プロパン及びこれらの誘導体等が挙げられる。

【0018】本発明では2価以上の脂肪族アルコールを用いることにより、ポリエステル樹脂の分子鎖がフレキシブルとなり、そのようなポリエステル樹脂を用いたトナーをキャリアと混合して二成分現像剤として用いた場合、現像装置内でキャリアが受けるストレスを緩和する効果があり、キャリア表面の樹脂被覆相が剥離するのを防ぎ、結果として現像剤の寿命が延びるという効果が得られる。また、非磁性一成分現像用トナーとして用いた場合においても現像スリーブと帯電部材との間をトナーが通過する際に受けるシヤを緩和し、高耐久性の現像剤とすることができる。

【0019】更に、ポリエステル主鎖が軟質化することにより低温での定着性が改善される。さらに、定着・オフセット性能を改善する目的で、トナー中にワックスを添加することは一般的に用いられる手段であるが、本発明における2価以上の脂肪族アルコールを用いたポリエステル樹脂では特にワックス類との相溶性が良好であり、低温での定着性能及び耐オフセット性がさらに改良される。

【0020】したがって、上記芳香族ジオールは本発明の主旨を損なわない範囲で用いる必要がある。上記芳香族ジオールを用いる量は全アルコール成分に対して30モル%以下であることが望ましい。より好ましくは20モル%以下である。

【0021】また、本発明で用いるカルボン酸成分としては、ナフタレンジカルボン酸、及び/またはその低級アルキルエステルとして、ジメチルナフタレート、ジエチルナフタレート、ジブチルナフタレート等がより好適に用いられる。これらの化合物は全酸成分の1モル%以上を用いることが必要であり、より好ましくは5モル%以上である。

【0022】ナフタレン環構造を含むモノマーは樹脂のT<sub>g</sub>を上げるのに効果があり、樹脂の耐熱凝集性が向上する。特にアルコール成分として軟質の脂肪族アルコールを主体に用いた系においては、樹脂のT<sub>g</sub>の低下を抑えることができ、2価以上の脂肪族アルコールを用いることによる低温定着性とナフタレンジカルボン酸による耐熱凝集性の両方を併せ持つ樹脂を得ることができる。

【0023】本発明におけるポリエステル樹脂は、例えば触媒の存在下で上記の原料成分(A)(B)を用いて脱水縮合反応或いはエステル交換反応を行うことにより得ることができる。この際の反応温度及び反応時間は、特に限定されるものではないが、通常150~300℃で2~24時間である。

【0024】このようなポリエステル樹脂の合成は、触



媒を添加して行うこともできる。使用するエステル化触媒としては、例えば、ジブチル錫ジラウレート、ジブチル錫オキサイドのごとき有機金属や、テトラブチルチタネートのごとき金属アルコキシドなどが挙げられる。また、使用するカルボン酸成分が低級アルキルエステルである場合には、エステル交換触媒を使用することができる。エステル交換触媒としては、例えば、酢酸亜鉛、酢酸鉛、酢酸マグネシウムのごとき金属酢酸塩、あるいは、酸化亜鉛、酸化アンチモンのごとき金属酸化物、又は、テトラブチルチタネートのごとき金属アルコキシド、などが挙げられる。触媒の添加量については、原材料の総量に対して0.01~1重量%の範囲とするのが好ましい。

【0025】本発明に用いられるポリエステル樹脂のガラス転移温度(T<sub>g</sub>)は50℃以上のものが好ましいが、中でも、そのT<sub>g</sub>が55℃以上のものが特に好ましい。T<sub>g</sub>が50℃以下ではトナーが保存、運搬、あるいはマシンの現像装置内部で高温下に晒された場合にブロッキング現象(熱凝集)を生じやすい。

【0026】また、本発明に使用されるポリエステル樹脂の軟化点としては、90℃以上、中でも、90℃~180℃の範囲のものが好ましい、より好ましくは、95℃~160℃の範囲である。軟化点が90℃未満の場合は、トナーが凝集現象を生じやすく、保存時や印字の際にトラブルになりやすく、180℃を越える場合には定着性が悪くなることが多い。

【0027】さらに、フルカラートナーとして、特に、色重ね時の色再現性やOHPシート上に定着させた際の透明性を要求される場合には、ポリエステル樹脂の軟化点としては、90℃~130℃の範囲のものが好ましい、より好ましくは、95℃~120℃の範囲である。

【0028】本発明のポリエステル樹脂の酸価としては、20mg KOH/g以下であることが、トナーの耐湿性が良好となる点で好ましい。

【0029】本発明における樹脂の軟化点は定荷重押し形細管式レオメータである島津製作所製フローテスタCFT-500を用いて測定されるT<sub>1</sub>/2温度で定義する。フローテスターでの測定条件は、ピストン断面積1cm<sup>2</sup>、シリンダ圧力0.98MPa、ダイ長さ1mm、ダイ穴径1mm、測定開始温度50℃、昇温速度6℃/min、試料重量1.5gの条件で行った。

【0030】本発明では前記式2、式3、式4、式5、式6、式7、式8で表される有機顔料の中から1種又はそれ以上を選択して使用するが、これらの顔料を使用することにより従来のトナーで通常用いられてきたマゼンタ顔料、例えばC. I. Pigment Red 57:1やキナクリドン顔料であるC. I. Pigment Red 122等に比較して良好な着色力、階調性、解像性及び転写特性を有するカラートナーを得ることができる。また、連続印刷した際に安定な帯電挙動を

示し、色再現性、透明性に優れた高画質画像の印刷を行うことができる。

【0031】なお、上記有機顔料のカラーインデックス番号は次の通りである。

式2の有機顔料; C. I. Pigment Red 150

式3の有機顔料; C. I. Pigment Red 31

式4の有機顔料; C. I. Pigment Red 147

式5の有機顔料; C. I. Pigment Red 176

式6の有機顔料; C. I. Pigment Red 187

式7の有機顔料; C. I. Pigment Red 188

式8の有機顔料; C. I. Pigment Red 269

本発明においては、上記の中でも式2及び/又は式8で表される有機顔料を使用することが好ましい。また、式2で表される有機顔料を使用することがより好ましい。

【0032】本発明における式2、式3、式4、式5、式6、式7、式8で表される有機顔料の使用量は、バインダー樹脂100重量部当たり1~50重量部の範囲が好ましく、2~30重量部の範囲がより好ましく、2~20重量部の範囲が特に好ましい。

【0033】本発明では上記の有機顔料に加えて、本発明の効果を失わない範囲において、色相を調整するための着色剤を添加して用いることができる。そのような着色剤としては、周知のものがあげられるが、例えば青系の着色剤としてはフタロシアニン系のC. I. Pigment Blue 15-3、インダンスロン系のC. I. Pigment Blue 60等が、赤系の着色剤としてはキナクリドン系のC. I. Pigment Red 122、アゾ系のC. I. Pigment Red 22、C. I. Pigment Red 23、C. I. Pigment Red 31、C. I. Pigment Red 48:1、C. I. Pigment Red 48:3、C. I. Pigment Red 57:1等が黄系の着色剤としてはアゾ系のC. I. Pigment Yellow 12、C. I. Pigment Yellow 13、C. I. Pigment Yellow 14、C. I. Pigment Yellow 17、C. I. Pigment Yellow 97、C. I. Pigment Yellow 155、ベンズイミダゾロン系のC. I. Pigment Yellow 151、C. I. Pigment Yellow 154、C. I. Pigment Yellow 180、等がある。

【0034】以上挙げた顔料は本発明の目的を損なわな

い範囲で式2～式8の有機顔料と併用することができる。例えば、黄色系顔料と組み合わせることにより橙黄色系のトナーにすることもできるし、シアン色系顔料と組み合わせることにより青紫色系のトナーとすることもできる。特に、C. I. Pigment Red 12、C. I. Pigment Red 23、C. I. Pigment Red 31等の青みの赤色顔料と併用することにより、着色力のある、鮮明なマゼンタ色を有するマゼンタトナーを得ることができる。

【0035】式2～式8の顔料と他の顔料を併用する場合は、式2～式8の顔料の使用量は顔料全体の含有量に対して40重量%以上が好ましく、より好ましくは50重量%以上である。

【0036】また、本発明のトナーにはこれまで公知の種々のワックス、例えばポリプロピレンワックス、ポリエチレンワックス、ポリアミド系ワックス、フィッシュートロプシュワックス等を離型剤として適宜用いることができるが、中でも高級脂肪酸エステル化合物及び／又は脂肪酸アルコール化合物を含有するワックスを離型剤として用いることが好ましい。

【0037】高級脂肪酸エステル化合物及び／又は脂肪酸アルコール化合物を含有するワックスの中でも、カルナウバワックス、モンタン系エステルワックス、ライスワックス、カイガラシワックス等の天然ワックス、及び／または合成エステル系ワックスが特に好ましい。合成エステル系ワックスとしてはペンタエリスリトールのテトラベネン酸エステルが特に好ましい。

【0038】これらのワックスは特にポリエステル樹脂に良好な分散性を示し、定着性、耐オフセット性の改善が顕著である。また、更に、これらのワックスは多数枚、長時間の印刷においても、例えば非磁性一成分現像用トナーとして用いた場合、現像スリーブに押しつけられた帯電部材に付着することなく、トナーに安定した帯電を与え、画像欠陥や地汚れ等が無く、高品位かつ高精細な画像の印刷が可能となる。さらに、本発明で使用する前記式2～式8から選択される1種又はそれ以上の有機顔料と共に用いてカラートナーとした場合、ポリプロピレンワックスのような炭化水素系のワックスと比較して透明性に優れたカラートナーが得られる。このような特性を有するカラートナーは、透明性があり、鮮やかな投影画像が求められるOHPシートへの印刷、および2色以上を重ねて印刷して良好な色再現性の中間色を印刷する用途に適している。

【0039】カルナウバワックスとしては精製により遊離脂肪酸を除去した脱遊離脂肪酸型カルナウバワックスを用いることが好ましい。脱遊離脂肪酸型カルナウバワックスの酸価としては3以下が好ましく、より好ましくは酸価2以下である。脱遊離脂肪酸型カルナウバワックスは従来のカルナウバワックスより微結晶となりポリエステル樹脂中での分散性が向上する。モンタン系エステ

ルワックスは鉱物より精製されたものであり、精製によりカルナウバワックスと同様に微結晶となりポリエステル樹脂中での分散性が向上する。モンタン系エステルワックスでは酸価として特に30以下であることが好ましい。また、ライスワックスは米ぬか口を精製したものであり、酸価は13以下であることが好ましい。カイガラシワックスはカイガラシ（別名イボタロウムシ）の幼虫が分泌する蠟状成分を、例えば、熱湯に溶かし、上層を分離後冷却固化して、あるいはそれを繰返すことにより得ることができる。このような手段により精製されたカイガラシワックスは固体状態において白色であり、極めてシャープな融点を示し本発明におけるトナー用ワックスとして適している。精製により酸価は10以下となり、トナー用として好ましいのは5以下である。

【0040】上記ワックスは単独で用いても組み合わせる用いても良く、バインダー樹脂に対して0.3～40重量部、好ましくは1～30重量部含有させることにより良好な定着オフセット性能が得られる。より好ましくは1～20重量部である。0.3重量部より少ないと耐オフセット性が損なわれ、40重量部より多いとトナーの流動性が悪くなり、また、二成分現像方式においてはキャリア表面に付着することによりスベントキャリアが発生し、トナーの帯電特性に悪影響を与えたり、非磁性一成分現像方式においては現像ロールに圧接された層厚規制部材に付着したりすることになる。

【0041】本発明では必要に応じて帯電制御剤を用いることができる。例えば正帯電制御剤としてニグロシン系染料、トリフェニルメタン系染料、4級アンモニウム塩、4級アンモニウム基及び／又はアミノ基を含有する樹脂等が、負帯電制御剤としてトリメチルエタン系染料、サリチル酸の金属錯塩、ベンジル酸の金属錯塩、銅フタロシアニン、ペリレン、キナクリドン、アゾ系顔料、金属錯塩アゾ系染料、アゾクロムコンプレックス等の重金属含有酸性染料、カリックスアレン型のフェノール系縮合物、環状ポリサッカライド、カルボキシル基及び／又はスルホン基を含有する樹脂、等がある。

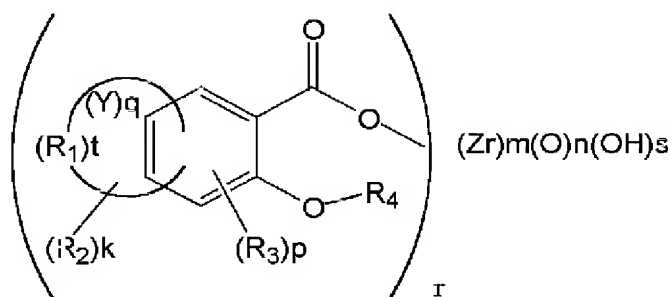
【0042】特に、本発明においては、無色の帯電制御剤を使用するのが望ましく、負の帯電制御剤としてはサリチル酸の金属錯化合物としてオリエント化学社製「ボントロンE-84」、保土ヶ谷化学社製「TN105」、クラリアント社製「N4PVP-2481」等が、また、無色の正帯電制御剤としては4級アンモニウム塩構造のTP-302、TP-415、TP-610；（保土谷化学製）、ボントロンP-51；（オリエント化学製）、コピーチャージPSY（クラリアントジャパン）等が好適に用いられる。また、4級アンモニウム基及び／又はアミノ基を含有する正帯電性の樹脂型帯電制御剤としては、「FCA-201-PS」（藤倉化成（株））等が挙げられる。

【0043】中でも、本発明において特に好適に用いることができる帯電制御剤としては、下記式9の化合物、及び式10の化合物がある。

<式9>

【0044】

【化17】



(式中、 $R_1$  は4級炭素、メチン、メチレンであり、N、S、O、Pのヘテロ原子を含んでいてもよく、Yは飽和結合又は不飽和結合で結ばれた環状構造を表し、 $R_2$ 、 $R_3$  は相互に独立してアルキル基、アルケニル基、アルコキシ基、置換基を有しても良いアリール基又はアリールオキシ基又はアラルキル基又はアラルキルオキシ基、ハロゲン基、水素、水酸基、置換基を有しても良いアミノ基、カルボキシル基、カルボニル基、ニトロ基、ニトロソ基、スルホニル基、シアノ基を表し、 $R_4$  は水素又はアルキル基を表し、tは0ないし1から12の整数、mは1から20の整数、nは0ないし1から20の整数、kは0ないし1から4の整数、pは0ないし1から4の整数、qは0ないし1から3の整数、rは1から20の整数、sは0又は1ないし20の整数である。)

(式中、 $R_1$  および $R_4$  は水素原子、アルキル基、置換又は非置換の芳香環(縮合環も含む)を示し、 $R_2$  および $R_3$  は置換又は非置換の芳香環(縮合環も含む)を示し、MはB、Al、Fe、Ti、Co、Crから選ばれる1種の3価の金属を示し、 $X^+$  はカチオンを示す)

【0047】<式9>の化合物の具体的な例としては、以下の<帯電制御剤1>~<帯電制御剤3>がある。

【0048】<帯電制御剤1>

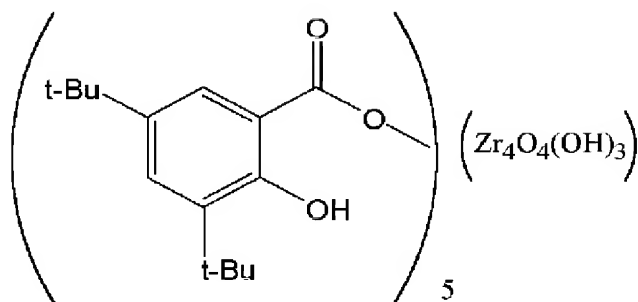
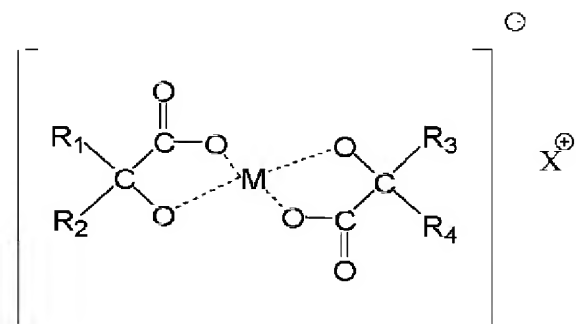
【0049】

【化19】

【0045】<式10>

【0046】

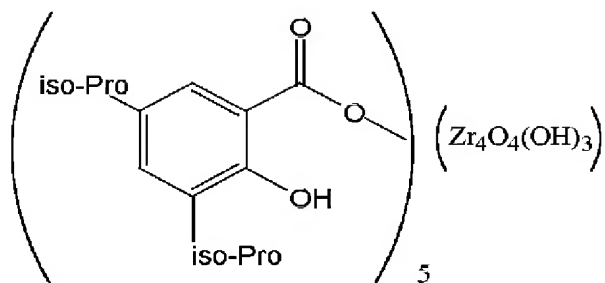
【化18】



【0050】<帯電制御剤2>

【化20】

【0051】



【0054】また、＜式10＞の化合物の具体的な例としては、以下の＜帯電制御剤4＞、＜帯電制御剤5＞がある。

【0055】＜帯電制御剤4＞

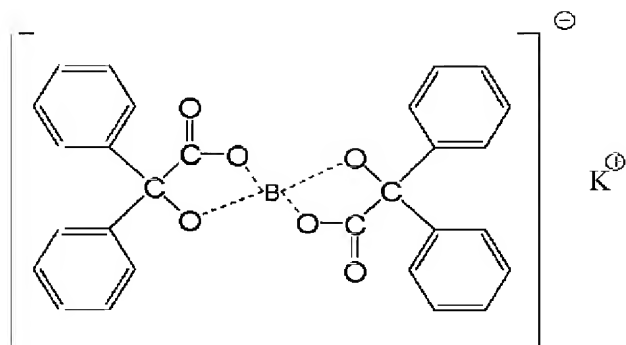
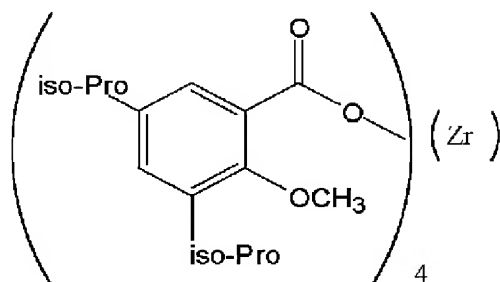
【0056】

【化22】

【0052】＜帯電制御剤3＞

【0053】

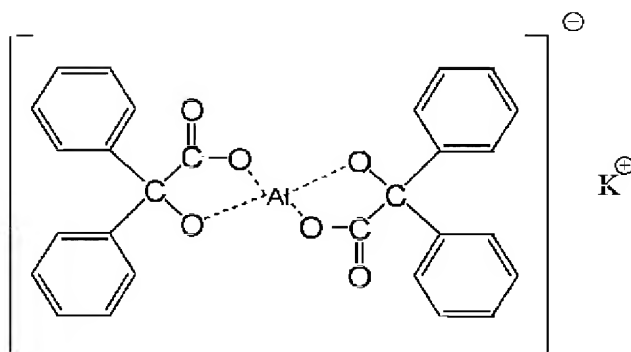
【化21】



【0057】＜帯電制御剤5＞

【化23】

【0058】



【0059】上記の帯電制御剤は単独で用いても組み合わせて用いても良く、バインダー樹脂に対して0.3～1.5重量部、好ましくは0.5～5重量部含有させることにより良好な帯電性能が得られる。

【0060】本発明のトナーを得るための製造方法は、

公知慣用の任意の手段に依って得る事ができるが、例えば樹脂と着色剤と必要に応じてワックス、各種添加剤を樹脂の融点（軟化点）以上で溶融混練した後、粉碎し、分級することにより得ることが出来る。本発明の効果をより一層発現させるためには、前記式2～式8から選択

される1種又はそれ以上の有機顔料を使用するバインダー樹脂の一部を高濃度で分散させて、その後、この分散物を使用するバインダー樹脂に希釈分散させると良い。

【0061】このように、着色剤を高濃度で予めバインダー樹脂に分散させる工程としては、従来公知の方法、即ち、マスターバッチ法やフラッシング法等を用いることができる。マスターバッチ法は、ニーダーやロールミルを用いて、着色剤を高濃度で樹脂とともに高シェアをかけて混練することにより良好な分散物を得る方法である。フラッシング法は、顔料の含水ペーストとバインダー樹脂とを、加圧ニーダーで加熱混練し、水とバインダー樹脂を置換し、水分を除去しながら高顔料濃度の分散物を得る方法である。

【0062】この高顔料濃度の分散物におけるバインダー樹脂、及び着色剤の割合は、バインダー樹脂100重量部に対して着色材量が10重量部～100重量部にあるのが好ましい。

【0063】具体的には例えば、上記の樹脂と着色剤とを必須成分として、2本ロール、3本ロール、加圧ニーダー、又は2軸押し出し機等の混練手段により混合する。この際、樹脂中に着色剤が均一に分散すればよく、その溶融混練の条件は特に限定されるものではないが、通常80～180℃で10分～2時間である。

【0064】また、必要に応じて、微粉碎工程における負荷の軽減及び粉碎効率の向上を目的とした粗粉碎を行う。粗粉碎に使用する装置、条件は特に限定されるものではないが、ロートプレックス、パルペライザー等により3mmメッシュパス以下の粒径に粗粉碎するのが一般的である。

【0065】次いで、ターボミル、クリプトロン等の機械式粉碎機、渦巻き式ジェットミルカウンタージェットミル、衝突板式ジェットミル等のエアード式粉碎機で微粉碎し、風力分級機等により分級するという方法が挙げられる。微粉碎、及び分級の装置、条件は所望の粒径、粒径分布、粒子形状になるように選択、設定すれば良い。

【0066】本発明では、トナーの流動性向上、帯電特性改良などトナーの表面改質のために種々の添加剤（外添剤と呼ぶ）を用いることができる。本発明で用いることのできる外添剤としては、例えば二酸化珪素、酸化チタン、酸化アルミ、酸化セリウム、酸化亜鉛、酸化錫、酸化ジルコニウム等の無機微粉体及びそれらをシリコンオイル、シランカップリング剤などの疎水化処理剤で表面処理したもの、ポリスチレン、アクリル、スチレンアクリル、ポリエステル、ポリオレフィン、セルローズ、ポリウレタン、ベンゾグアナミン、メラミン、ナイロン、シリコン、フェノール、フッ化ビニリデン等の樹脂微粉体等が用いられる。

【0067】これらの中でも各種のポリオルガノシロキサンやヘキサメチレンジシラザンやシランカップリング剤等で表面を疎水化処理した二酸化珪素（シリカ）が特

に好適に用いることができる。そのようなものとして、例えば、次のような商品名で市販されているものがある。

【0068】AEROSIL R972, R974, R202, R805, R812, RX200, RY200, R809, RX50, RA200HS, RA200H〔日本アエロジル（株）〕  
WACKER HDK H2000, H1018, H2050EP, HDKH3050EP, HVK2150〔ワッカーケミカルズイーストアジア（株）〕  
Nipsil SS-10, SS-15, SS-20, SS-50, SS-60, SS-100, SS-50B, SS-50F, SS-10F, SS-40, SS-70, SS-72F,〔日本シリカ工業（株）〕  
CABOSIL TG820F, TS-530, TS-720〔キャボット・スペシャルティ・ケミカルズ・インク〕

【0069】外添剤の粒子径は、トナーの直径の1/3以下であることが望ましく、特に好適には1/10以下である。また、これらの外添剤は、異なる平均粒子径の2種以上を併用してもよい。

【0070】特に非磁性一成分現像用トナーにおいては、粒子径大のものと粒子径小のものとを併用することにより、トナー流動性及び現像耐久性を向上させ、現像機のブレードへの固着及びカブリの防止、ランニング時における帯電の長期安定性等が得られ、好ましい。

【0071】外添剤の使用割合は母体トナー100重量部に対して、0.05～5重量%、好ましくは0.1～3重量%である。

【0072】前記シリカを、トナー粒子に外添させる方法としては、例えば通常の粉体用混合機であるヘンシェルミキサーなどや、ハイブリダイザー等のいわゆる表面改質機を用いて行うことができる。尚、この外添処理は、トナー粒子の表面にシリカが付着させるようにしても良いし、シリカの一部がトナー粒子に埋め込まれるようにしても良い。

【0073】本発明の静電荷現像用カラートナーは、電子写真法による静電潜像の現像用として、一成分現像剤、非磁性一成分現像剤あるいはキャリアと混合した二成分現像剤として使用できる。キャリアの種類には特に制限はなく、公知慣用の鉄粉、フェライト、マグネタイト等やそれらに樹脂コートしたキャリアが用いられる。

【0074】キャリアのコア剤は通常の二成分現像方式に用いられる鉄粉、マグネタイト、フェライト等が使用できるが、中でも真比重が低く、高抵抗であり、環境安定性に優れ、球形にし易いため流動性が良好なフェライト、またはマグネタイトが好適に用いられる。コア剤の形状は球形、不定形等、特に差し支えなく使用できる。平均粒径は一般的には10～500μmであるが、高解像度画像を印刷するためには30～80μmが好まし

い。

【0075】また、これらのコア剤を被覆するコーティング樹脂としては、例えばポリエチレン、ポリプロピレン、ポリスチレン、ポリアクリロニトリル、ポリビニルアセテート、ポリビニルアルコール、ポリ塩化ビニル、ポリビニルカルバゾール、ポリビニルエーテル、ポリビニルケトン、塩化ビニル／酢酸ビニル共重合体、スチレン／アクリル共重合体、オルガノシロキサン結合からなるストレートシリコン樹脂あるいはその変性品、フッ素樹脂、(メタ)アクリル樹脂、ポリエステル、ポリウレタン、ポリカーボネート、フェノール樹脂、アミノ樹脂、メラミン樹脂、ベンゾグアナミン樹脂、ユリア樹脂、アミド樹脂、エポキシ樹脂、アクリルポリオール樹脂等が使用できる。これらの中でも、特にシリコン樹脂、フッ素樹脂、(メタ)アクリル樹脂が帯電安定性、被覆強度等に優れ、より好適に使用し得る。つまり本発明で用いられる樹脂被覆キャリアは、コア剤としてフェライト、あるいはマグネタイトを用い、シリコン樹脂、フッ素樹脂、(メタ)アクリル樹脂から選ばれる1種以上の樹脂で被覆された樹脂被覆磁性キャリアであることが好ましい。

【0076】本発明の静電荷像現像用カートナーを非磁性一成分現像用トナーとして用いる場合、接触型の非磁性一成分現像用トナーとして用いるのが好ましい。接触型の非磁性一成分現像方法とは、トナーが現像スリーブとそれに圧接された層厚規制部材との間を通過することにより摩擦帯電し、次いで感光体の表面に形成された静電潜像を現像する方法である。

【0077】この場合、通常の使用条件であれば特に現像装置の帯電付与部材の材質等を限定するものではない。例えばアルミニウム、ステンレス、ウレタンゴム、シリコンゴム製の現像スリーブ、アルミニウム、ステンレス、ジュラルミン、銅、あるいはそれらにウレタンゴム、シリコンゴムを貼り合わせた層厚規制部材等が好適に使用できる。

【0078】また、非磁性一成分現像用トナーとして用いた場合に、本発明の静電荷像現像用カートナーが効果を発現するために適した現像装置の構成は、現像スリーブと層厚規制部材とのいずれか一方がアルミニウム、

(合成例3)

ポリオキシエチレンー(2.0)ー2,2-ビス(4-ヒドロキシフェニル)プロパン	64重量部
イソフタル酸	16重量部
テレフタル酸	16重量部
無水マレイン酸	0.6重量部
ジブチル錫オキシド	0.06重量部

以上の原料をガラス製2Lの四ツ口フラスコに入れ温度計、攪拌棒及び窒素導入管を取り付け、電熱マントルヒーター中で、常圧窒素気流下にて230℃で24時間反応後、順次減圧し、10mmHgで反応を続行した。反

ステンレス等の金属である場合であり、最も有効な組み合わせ(現像スリーブ／層厚規制部材)は、ウレタンゴムまたはシリコンゴム製の現像スリーブとステンレス製の層厚規制部材の組み合わせ、またはステンレス製の現像スリーブとウレタンゴムまたはシリコンゴム製の層厚規制部材の組み合わせである。

【0079】

【実施例】以下、実施例及び比較例を用いて、本発明を更に詳細に説明する。なお、以下において、組成表内の数値は『重量部』を表わす。最初にトナーを調製するにあたって用いたバインダー樹脂の合成例を下記に示す。

(合成例1)

ナフタレンジカルボン酸	87重量部
テレフタル酸	249重量部
ジエチレングリコール	26重量部
ネオペンチルグリコール	104重量部
エチレングリコール	50重量部
テトラブチルチタネート	2.5重量部

以上の原料をガラス製2Lの四ツ口フラスコに入れ温度計、攪拌棒及び窒素導入管を取り付け、電熱マントルヒーター中で、常圧窒素気流下にて240℃で10時間反応後、順次減圧し、10mmHgで反応を続行した。反応はASTM・E28-517に準じる軟化点により追跡し、軟化点が101℃に達した時反応を終了した。得られた重合体(以下、樹脂Aと表す)は、無色の固体であり、酸価7、DSC測定法によるガラス転移温度70℃、軟化点は102℃であった。

【0080】(合成例2)

テレフタル酸	315重量部
ジエチレングリコール	21重量部
シクロヘキサジメタノール	144重量部
エチレングリコール	50重量部
テトラブチルチタネート	2.5重量部

以上の原料を用いて樹脂合成例1と同様に反応を行った。得られた重合体(以下、樹脂Bと表す)は、無色の固体であり、酸価9、DSC測定法によるガラス転移温度60℃、軟化点が97℃であった。

【0081】

反応はASTM・E28-517に準じる軟化点により追跡し、軟化点が99℃に達した時反応を終了した。

【0082】得られた重合体(以下、樹脂Cと表す)は、無色の固体であり、酸価7、DSC測定法によるガ

ラス転移温度62℃、軟化点が101℃であった。

( 合成例4 )

テレフタル酸	332重量部
イソフタル酸	332重量部
ポリオキシプロピレン(2,2)-2,2-ビス(4-ヒドロキシフェニル)プロパン	700重量部
トリメチロールプロパン	80重量部
エチレングリコール	75重量部
テトラブチルチタネート	3重量部

上記配合物を攪拌器、コンデンサー、温度計をセットした四つ口フラスコに入れ、窒素ガス気流下、脱水縮合により生成した水を除去しながら、240℃にて10時間常圧で反応させた。その後順次減圧し10mmHgで反応を続行した。反応は軟化点により追跡し、軟化点が151℃に達した時反応を終了した。得られた重合体(以下、樹脂Dと表す)の軟化点は153℃、酸価は4、DSC測定法によるTgは65℃であった。

【0084】( 合成例5 )

イソフタル酸	116重量部
テレフタル酸	166重量部
無水トリメリット酸	38重量部
ジエチレングリコール	26重量部
ネオペンチルグリコール	104重量部
エチレングリコール	50重量部
テトラブチルチタネート	2.5重量部

以上の原料をガラス製2Lの四つ口フラスコに入れ温度

<加工顔料の製造例>

( 加工顔料1 )

樹脂A

<式2>の有機顔料

650重量部

350重量部

以上の原料をヘンシェルミキサーにて混合後、加熱二本ロールにて混練した。冷却後粗粉砕を行い、顔料含有率35%の加工顔料1を作製した。

【0087】( 加工顔料2 ) 加工顔料1の作製における樹脂Aを樹脂Bとする以外は加工顔料1を作製する場合と全く同様にして加工顔料2を作製した。

【0088】( 加工顔料3 ) 加工顔料1の作製における式2の有機顔料を式8の有機顔料とする以外は加工顔料1を作製する場合と全く同様にして加工顔料3を作製した。

【0089】( 加工顔料4 ) 加工顔料1の作製における樹脂Aを樹脂Eとする以外は加工顔料1を作製する場合と全く同様にして加工顔料4を作製した。

【0090】( 比較用加工顔料1 ) 加工顔料1の作製における樹脂Aを樹脂Cとする以外は加工顔料1を作製する場合と全く同様にして比較用加工顔料1を作製した。

【0091】( 比較用加工顔料2 ) 加工顔料1の作製における樹脂Aを樹脂Dとする以外は加工顔料1を作製する場合と全く同様にして比較用加工顔料2を作製した。

【0092】( 比較用加工顔料3 ) 上記の加工顔料1に

【0083】

計、攪拌棒及び窒素導入管を取り付け、電熱マントルヒーター中で、常圧窒素気流下にて240℃で10時間反応後、順次減圧し、10mmHgで反応を続行した。反応はASTM-E28-517に準じる軟化点により追跡し、軟化点が148℃に達した時反応を終了した。得られた重合体(以下、樹脂Eと表す)は、無色の固体であり、酸価4、DSC測定法によるガラス転移温度72℃、軟化点は151℃であった。

【0085】樹脂の軟化点は定荷重押し形細管式レオメータである島津製作所製フローテスタCF-T-500を用いて測定されるT1/2温度で定義する。フローテスターでの測定条件は、ピストン断面積1cm<sup>2</sup>、シリンダ圧力0.98MPa、ダイ長さ1mm、ダイ穴径1mm、測定開始温度50℃、昇温速度6℃/min、試料重量1.5gの条件で行った。

【0086】

において、式2の有機顔料の代わりに、C. I. ピグメントレッド122を用いた以外は、同様にして比較用加工顔料3を得た。

【0093】( 比較用加工顔料4 ) 上記加工顔料1において、式2の有機顔料の代わりに、C. I. ピグメントレッド57:1を用いた以外は、同様にして比較用加工顔料4を得た。

【0094】( 比較用加工顔料5 ) 上記の加工顔料4において、式2の有機顔料の代わりに、C. I. ピグメントレッド122を用いた以外は、同様にして比較用加工顔料5を得た。

【0095】( 比較用加工顔料6 ) 上記加工顔料4において、式2の有機顔料の代わりに、C. I. ピグメントレッド57:1を用いた以外は、同様にして比較用加工顔料6を得た。

【0096】( 実施例1 ) 樹脂A93重量部、式2の顔料(Carmin 190(有本化学社製))4重量部、帯電制御剤(前記<帯電制御剤4>の化合物、LR-147(日本カーリット社製))1重量部、カルナバワックス(精製カルナバワックスNo. 1、酸価5、セ

ラリカNODA（株）製）2重量部をヘンシェルミキサーで混合し、2軸混練機で熔融混練し、冷却後ジェットミルにて微粉碎し、分級して平均粒径8.0 $\mu$ mのトナーを作製した

【0097】次に、このトナー100重量部に対し、日本アエロジル製シリカ「NAX50」1重量部、「RY-200」1重量部を外添することにより、実施例1のマゼンタトナーを得た。

【0098】同様にして、表1に示す組成で樹脂、有機顔料（あるいは加工顔料）、帯電制御剤、WAXを、ヘンシェルミキサーで十分に混合した後、2軸混練機で熔融混練して、冷却後、粉碎、分級することにより、トナーを製造して、更に実施例1と同様に外添工程を行うことにより実施例2～8、比較例1～5のトナーを得た。

【0099】

【表1】

表1	樹脂	着色剤	WAX	帯電制御剤	体積平均 ( $\mu$ m)
実施例1	樹脂A 93部	式2の顔料 4部	加ナバWAX 2部	帯電制御剤4 1部	8.0
実施例2	樹脂A 85部	加工顔料1 12部	加ナバWAX 2部	帯電制御剤4 1部	7.8
実施例3	樹脂B 85部	加工顔料2 12部	加ナバWAX 2部	帯電制御剤1 1部	7.8
実施例4	樹脂A 85部	加工顔料3 12部	加ナバWAX 2部	帯電制御剤4 1部	7.8
実施例5	樹脂A 85部	加工顔料1 12部	PPWAX 2部	帯電制御剤4 1部	8.1
実施例6	樹脂A 85部	加工顔料1 12部	加ナバWAX 2部	E-84 1部	8.0
実施例7	樹脂B 85部	加工顔料2 12部	PETB 2部	帯電制御剤4 1部	7.8
実施例8	樹脂A 85部	加工顔料3 12部	PETB 2部	帯電制御剤4 1部	8.0
比較例1	樹脂A 92部	P.R.122 5部	加ナバWAX 2部	帯電制御剤4 1部	7.8
比較例2	樹脂A 93部	P.R.57:1 4部	加ナバWAX 2部	帯電制御剤4 1部	7.9
比較例3	樹脂C 85部	比較用加工顔料1 12部	加ナバWAX 2部	帯電制御剤4 1部	7.9
比較例4	樹脂A 85部	比較用加工顔料3 12部	加ナバWAX 2部	帯電制御剤4 1部	7.9
比較例5	樹脂A 85部	比較用加工顔料4 12部	加ナバWAX 2部	帯電制御剤4 1部	8.0

【0100】表1中の略号は以下の通り。また、部は重量部を表す。

- ・P.R.122；C.I.ピグメントレッド122（Fastogen Super Magenta R「大日本インキ化学工業（株）製」）
- ・P.R.57：1；C.I.ピグメントレッド57：1（Symuler Brilliant Carmin 6B 285「大日本インキ化学工業（株）製」）
- ・PETB；ペンタエリスリトールのテトラベヘン酸エステル・カルナバワックス；精製カルナバワックスNo.1（酸価5、セラリカNODA（株）製）
- ・PPWAX；ビスコール660P（ポリプロピレンワックス「三洋化成製」）
- ・E-84；ポントロンE-84（サリチル酸の金属錯化合物「オリエント化学社製」）

【0101】（表1のトナーの評価）市販の非磁性一成分現像方式のプリンター（リコー（株）製「イプシオカラー2000」）のカートリッジから専用トナーを抜き、洗浄したカートリッジに、表1に示した実施例及び比較例のトナーを充填し、画像濃度5%で10000枚の連続印字を行った。環境条件の変動に対する印字画像の安定性を評価するために、25℃、50%と32℃、

85%の2つの環境下で連続印字試験を実施した。

【0102】（1）画像濃度・地汚れ・帯電量  
印刷物の画像濃度及び地汚れは、マクベス濃度計RD-918で測定した。なお、地汚れは印刷後の白地部濃度からプリント前白紙濃度を差し引いて求めた。その差が0.01未満の時を○、0.01～0.03未満の時を△、0.03以上の時を×とした。また、印字トナーの帯電量を、吸引式小型帯電量測定装置Mode210HS（トレック社製）を用いて測定した。

【0103】（2）トナー落ち・トナー飛散

10000枚印字後、カートリッジに装着された現像スリーブからトナーがこぼれ落ちたり（トナー落ち）、現像装置の周辺に飛び散って（トナー飛散）マシン内部を汚したりしない状態を○、少量のトナー落ち、あるいはトナー飛散が認められる状態を△、多量のトナー落ち、あるいはトナー飛散が認められる状態を×と判定した。

【0104】（3）OHP透明性

上記プリンターを用いて、OHPシート上に未定着画像を形成し、上記の定着・オフセット試験で使用した定着ユニットにより140℃にて未定着画像の定着を行った。

【0105】以上の手順により作成したOHPシートを、オーバーヘッドプロジェクターにて白色のスクリー



ンに投影し鮮明度の評価を行った。評価は目視で行い、鮮明で透明性のある良好な投影画像であれば○、やや透明性に欠け若干の濁りがある場合を△、濁りのある黒みがあった投影画像であれば×とした。

【0106】25℃、50%における結果を表2に、32℃、85%における結果を表3に示す。

【0107】

【表2】

表2

	トナー落ちトナー飛散 初期/10000枚	画像濃度 初期/10000枚	地汚れ 初期/10000枚	帯電量 ( $\mu\text{C/g}$ )	OHP 透明性
実施例1	○/△	1.39/1.42	○/○	10.5	△
実施例2	○/○	1.37/1.39	○/○	12.0	○
実施例3	○/○	1.39/1.42	○/○	12.8	○
実施例4	○/○	1.38/1.41	○/○	12.7	○
実施例5	○/○	1.36/1.39	○/○	13.8	○
実施例6	○/△	1.40/1.46	○/○	10.0	○
実施例7	○/○	1.36/1.37	○/○	12.5	○
実施例8	○/○	1.39/1.41	○/○	12.5	○
比較例1	△/×	1.33/1.69	○/△	-8.5	×
比較例2	○/×	1.38/1.48	△/×	-9.2	△
比較例3	○/○	1.38/1.41	○/○	12.3	○
比較例4	○/△	1.33/1.46	○/△	-9.8	○
比較例5	○/△	1.33/1.45	○/△	-9.7	○

【0108】

【表3】

表3

	トナー落ちトナー飛散 初期/10000枚	画像濃度 初期/10000枚	地汚れ 初期/10000枚	帯電量 ( $\mu\text{C/g}$ )	OHP 透明性
実施例1	○/△	1.36/1.30	○/○	-9.5	△
実施例2	○/○	1.34/1.30	○/○	-11.1	○
実施例3	○/○	1.36/1.31	○/○	-12.3	○
実施例4	○/○	1.35/1.31	○/○	-12.0	○
実施例5	○/○	1.33/1.28	○/○	-12.5	○
実施例6	○/△	1.38/1.44	○/○	-8.9	○
実施例7	○/○	1.33/1.30	○/○	-11.6	○
実施例8	○/○	1.37/1.33	○/○	-12.2	○
比較例1	△/×	1.28/1.22	○/×	-7.7	×
比較例2	○/×	1.32/1.10	△/×	-5.1	△
比較例3	○/△	1.35/1.25	○/△	-12.2	○
比較例4	○/×	1.28/1.16	○/×	-8.1	○
比較例5	○/×	1.27/1.16	○/×	-8.1	○

【0109】(4) ヒートロール定着による定着/オフセットテスト

市販の非磁性一成分現像方式のプリンターを改造したテスト機にてA-4紙サイズの未定着画像サンプルを作製し、下記仕様のヒートロール定着ユニットを用いて、下記のテスト条件にて定着開始温度、およびオフセット現象の有無を確認した。

ロール材質            上：四弗化エチレン  
                              下：HTVシリコン  
ロール形状            径：50mm  
                              長さ：370mm  
上ロール荷重           ：     7kg  
上/下ロールニップ幅   ：     4mm  
紙送り速度            ： 100mm/sec

定着開始温度を測定するため下記の式により計算される画像濃度残存比率を求めた。

【0110】画像濃度残存比率＝堅牢度試験後画像濃度/同左試験前画像濃度

\* 画像濃度はマクベス画像濃度計RD-918にて測定した。

\* 堅牢度試験後画像濃度とは、学振型摩擦堅牢度試験機（荷重：200g、擦り操作：5ストローク）を用いて定着画像を擦った後の画像濃度である。

画像濃度残存比率80%以上で実用上問題ないレベルとし、その最低温度を定着開始温度とした。

【0111】オフセット開始温度は定着画像サンプルを観察し、目視にてオフセット現象が認められる温度とした。結果を表4に示した。

【0112】

【表4】

表4

	定着開始温度/オフセット開始温度 ℃
実施例1	130-210
実施例2	130-210
実施例3	125-210
実施例4	130-210
実施例5	140-210
実施例6	130-210
実施例7	125-210
実施例8	130-210
比較例1	130-210
比較例2	130-210
比較例3	140-210
比較例4	130-210
比較例5	130-210

【0113】（実施例9）樹脂E85重量部、加工顔料4を12重量部、帯電制御剤として4級アンモニウム塩

構造のTP-415（保土谷化学製）1重量部、カルナバワックス（精製カルナバワックスNo. 1、酸価5、セリカNODA（株）製）2重量部をヘンシェルミキサーで混合し、2軸混練機で熔融混練し、冷却後ジェットミルにて微粉碎し、分級して平均粒径8.0 $\mu$ mのトナーを作製した。

【0114】次に、このトナー100重量部に対し、キャボット・スペシャルティ・ケミカルズ・インク製シリカ「TG820F」1重量部を外添することにより、実施例9の正帯電性のマゼンタトナーを得た。次いで、このトナー5重量部とシリコン樹脂を被覆した平均粒

径80 $\mu$ mのフェライトキャリア95重量部とをボールミルにて混合し、二成分現像剤とした。

【0115】同様に、表5に示す組成で樹脂、有機顔料（あるいは加工顔料）、帯電制御剤、WAXを、ヘンシェルミキサーで十分に混合した後、2軸混練機で熔融混練して、冷却後、粉碎、分級することにより、トナーを製造して、更に実施例9と同様に外添工程を行うことにより比較例6～8のトナーを得た。

【0116】

【表5】

表5

	樹脂	着色剤	WAX	帯電制御剤	体積平均径 ( $\mu$ m)
実施例9	樹脂E 85部	加工顔料4 12部	カルバ <sup>®</sup> WAX 2部	TP-415 1部	8.0
比較例6	樹脂D 85部	比較用加工顔料2 12部	カルバ <sup>®</sup> WAX 2部	TP-415 1部	1.8
比較例7	樹脂E 85部	比較用加工顔料5 12部	カルバ <sup>®</sup> WAX 2部	TP-415 1部	1.9
比較例8	樹脂E 85部	比較用加工顔料6 12部	カルバ <sup>®</sup> WAX 2部	TP-415 1部	1.9

【0117】（表5のトナーの評価）

【0118】（1）印刷耐久テスト

表5の二成分現像剤により市販のレーザービームプリンター（セレン感光体搭載）を用いて25℃、50%、及び32℃、85%の条件下で、50000枚の印刷を行い、連続プリントの前後における画像部の濃度及び地汚れ濃度を測定すると共に、現像剤の帯電量を測定した。画像濃度及び地汚れはマクベス濃度計RD-918で測定した。なお、地汚れは印刷後の白地部濃度からプリント前白紙濃度を差し引いて求めた。その差が0.01未満の時を○、0.01～0.03未満の時を△、0.03以上の時を×とした。

【0119】また、50000枚印刷後における現像器

内部のトナーの飛散状況を目視観察した。飛散が全く観察されない状態を○、飛散がほとんど見えないが、装置内部をウエスで拭くとトナー汚れが観察される状態を△、機内飛散が目視で確認出来る状態を×、ひどい機内飛散が確認出来る状態を××とした。

【0120】帯電量については、トナーを現像装置内部から採取して、ブローオフ帯電量測定機（東芝ケミカル製）で測定した。

【0121】25℃、50%における結果を表6に、32℃、85%における結果を表7に示す。

【0122】

【表6】

表6

	画像濃度 初期/50000枚	地汚れ 初期/50000枚	帯電量 ( $\mu$ C/g)	トナーの飛散状況
実施例9	1.33/1.36	○/○	18.5	○
比較例6	1.32/1.38	○/○	16.8	○
比較例7	1.36/1.47	○/△	20.5	×
比較例8	1.35/1.46	○/△	16.5	×

【0123】

【表7】

表7

	画像濃度 初期/50000枚	地汚れ 初期/50000枚	帯電量 ( $\mu$ C/g)	トナーの飛散状況
実施例9	1.38/1.40	○/○	17.8	○
比較例6	1.35/1.43	○/△	14.8	△
比較例7	1.38/1.49	○/×	19.6	×
比較例8	1.37/1.47	○/×	15.8	×

【0124】（2）ヒートロール定着による定着/オフセットテスト

前記の方法を用いて未定着画像サンプルを作製し、前期と同様のヒートロール定着ユニットを用いて定着開始温度、およびオフセット開始温度を調べた。試験結果を表

8に示す。

【0125】

【表8】

表 8

	定着開始温度／オフセット開始温度 ℃
実施例	140-220
比較例	150-220
比較例	140-220
比較例	140-220

【 0 1 2 6 】

【発明の効果】本発明の静電荷像現像用カートナーは、優れた着色力及び色相を有し、温度、湿度等の環境が変動しても、安定した帯電特性を示す。それ故に、色再現性に優れ、また、帯電量が変動せず、良好かつ安定な印字画質を示す。また、低温定着、あるいは短時間定着のような低エネルギー定着条件においても良好な定着性を示し、耐オフセット性にも優れる。